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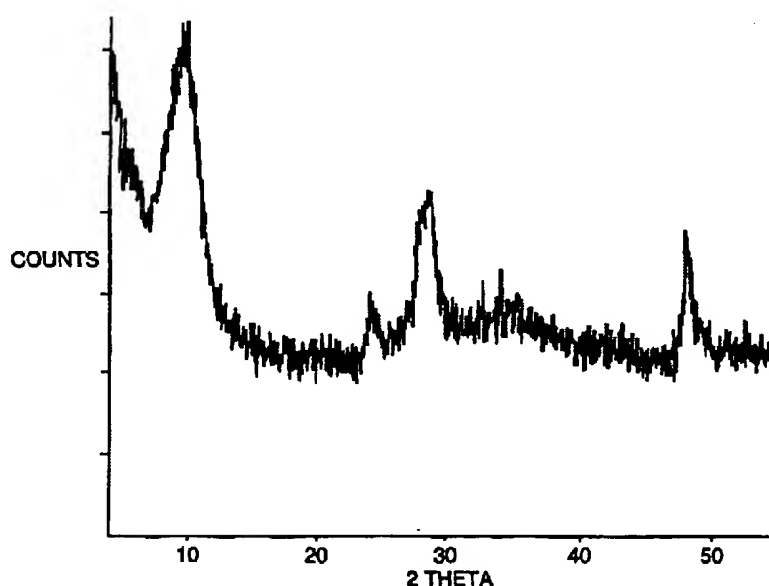
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(54) Title: PARTIALLY CRYSTALLINE LAYERED SODIUM TITANATE



(57) Abstract

This invention is a partially crystalline sodium ~~nonatitanate~~ strontium ion-exchange composition, having an X-ray diffraction d-spacing of from 8 to 9.9 angstroms, an X-ray diffraction 001 peak half-width greater than 1° and less than about 4.5°, and a strontium K_α greater than 20,000 mL/g.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention concerns a novel partially crystalline sodium nonatitanate composite having
5 a layered structure. The novel sodium titanate exhibits ion exchange properties, and it is particularly designed to be an excellent ion-exchanger for strontium.

(2) Description of the Art

Ever since nuclear weapons were first produced at the end of World War II, large
amounts of nuclear waste have been generated and stored at various facilities. The nuclear
10 waste, which consists largely of the byproducts of uranium and plutonium production and purification, was disposed of in ways which were deemed suitable at the time, but which in retrospect are now inadequate. Much of the nuclear waste is now stored in tanks as a highly alkaline mixture of salts and liquids which, if not recovered and properly remediated, will potentially create severe environmental problems.

15 Most of the stored aqueous nuclear waste is alkaline (pH 14), and contains high concentrations of sodium nitrate. The tanks contain various complexing agents, fission products, transuranic elements and other materials. Much of the stored nuclear waste is in the form of sludge created when alkali was added to the waste to prevent tank corrosion. Some of the radioactive material has been incorporated into salt cakes which is the evaporative product of
20 the alkaline aqueous material. It is desired to remove the radioactive elements from the waste in order to allow for subsequent safe disposal of the non-radioactive materials. The removal of two of the metallic radionuclides, cesium and strontium, is particularly important because their

half-lives are long enough to represent a hazard for an extended period of time.

Sodium nonatitanate is known as a strontium ion exchanger. J. Lehto; *J. Radioanal. Nucl. Chem. Letters*, **118**: 1-13 (1987) describes the ion exchange behavior of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ toward strontium. The sodium titanate was prepared hydrothermally at 300° C followed by
5 boiling with NaOH.

Other references that disclose the preparation and use of sodium titanates as strontium ion exchangers include R.G. Dosch, "Final Report on the Application of Titanates, Niobates, and Tantalates to Neutralized Defense Waste Contamination Materials Properties, Physical Forms and Regeneration Techniques; National Technical Information Service" (1981); R.M.
10 Merrill; *Journal of Radioanalytical Chemistry*; **43**: 93-100 (1978); J. Lehto et al.; *J. Chem. Soc. Dalton Trans.*, 101-103 (1989); and S.P. Mishra et al.; *J. Radioanalytical and Nuclear Chemistry, Articles*; **162**:2, 299-305 (1992).

Various types of sodium titanates are described in the prior art as well as various uses for sodium titanates as an ion exchanger for ions besides strontium. M. Watanabe; *Journal of*
15 *Solid State Chemistry*, **36**: 91-96 (1981) describes the preparation of sodium titanate compounds from hydrothermal reactions involving TiO_2 with NaOH. The titanates described were $\text{TiO}_2 \cdot \text{Na}_2\text{O} \cdot n\text{Ti}_2\text{Na}_x\text{TiO}_7$. J. Akimoto et al., *Journal of Solid State Chemistry*, **90**: 147-154 (1991) describes the synthesis of monosodium titanates $\text{NaTi}_4\text{O}_{13}$, which are distinct from the sodium nonatitanates disclosed here. H. Leinonen et al., *Reactive Polymers*, **23**: 221-228 (1994)
20 describes the use of sodium titanates as ion exchangers for nickel and zinc.

Lehto et al.; *Radiochem. Radioanal. Letters*, **50**:6, 375-384 (1982) describes the effects

of gamma radiation on sodium titanate and other solid ion exchangers. The study concluded that gamma radiation had very little impact on the strontium ion exchange capacity of sodium titanate.

5 PCT Application WO 94/19277 discloses silico-titanates and methods for making and using them. The silico-titanates disclosed are useful for removing cesium from radioactive wastes. U.S. Patent 4,156,646 discloses removal of plutonium and americium from aqueous alkaline waste solutions using sodium titanate ion exchangers. The sodium titanate used is a monosodium titanate.

10 U.S. Patent No. 5,352,644 describes a titania bound zeolite made by combining the zeolite, a low acidity titania binder material, and an aqueous slurry of titanium oxide hydrate.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a novel partially crystalline layered sodium titanate that exhibits superb ion exchange properties towards strontium.

5 It is another object of this invention to provide a novel partially crystalline layered sodium titanate that is capable of ion exchanging strontium under highly alkaline solutions.

It is still another object of this invention to provide a novel partially crystalline layered sodium titanate that has a d-spacing of from about 8 to about 9.9 angstroms.

It is yet another object of this invention to provide a novel method for preparing a sodium titanate.

10 In one embodiment, this invention is a partially crystalline layered sodium titanate having a d-spacing of from about 8 to about 9.5 angstroms.

In another embodiment, this invention is a partially crystalline layered sodium titanate having a d-spacing of from 9.0 to 9.9 angstroms, a Langmuir surface area of from about 60 to about 110 m²/g, and 001 reflection peak width greater than 1 degrees and less than about 4.5 degrees.

15 In still another embodiment, this invention is a partially crystalline layered sodium titanate composite having the x-ray diffraction pattern of Figure 1 prepared by hydrothermally treating a sodium titanate gel at a temperature of from about 120°C to about 200°C in the presence of aqueous NaOH for a period of time ranging from about 1 to about 20 hours.

20 In yet another embodiment, this invention is a partially crystalline layered sodium titanate having a d-spacing of from 9.0 to 9.9 angstroms, a 001 reflection peak width greater than 2

degrees and less than about 4.5 degrees prepared by the method comprising hydrothermally treating a sodium titanate gel prepared by a reflux method and then hydrothermally treating the reflux product at a temperature of from about 150°C to about 170 °C in the presence of added aqueous NaOH for a period of time ranging from about 1 hour to about 20 hours.

DESCRIPTION OF THE DRAWINGS

There is shown in the drawings a presently preferred embodiments of the layered partially crystalline sodium titanate of this invention wherein:

Figure 1 is an X-ray diffraction pattern of a layered partially crystalline sodium titanate composite of this invention having a d-spacing of 9.4 angstroms;

Figure 2 are X-ray diffraction patterns of partially crystalline layered sodium titanate samples 1-1 to 1-6 as prepared in Example 1;

Figure 3 are X-ray diffraction patterns of partially crystalline layered samples 1-7 to 1-13 as prepared in Example 1;

Figure 4 is an X-ray diffraction pattern of partially crystalline layered sodium titanate sample 2-1 prepared in Example 2.

Figure 5 is a plot of the log (K_d) versus pH for the uptake of strontium by sodium titanate;

Figure 6 is the X-ray diffraction pattern of dehydrated layered partially crystalline sodium titanate of this invention having a d-spacing of 9.00 angstroms as prepared in Example 9;

Figure 7 is the X-ray diffraction pattern of hydrated layered partially crystalline sodium titanate that has a d-spacing of 10.2 angstroms as prepared in Example 9;

Figure 8 is a plot of the strontium uptake of a partially crystalline layered sodium titanate prepared in Example 5 as a function of the full-width half maximum (FWHM) peak height of the 001 reflection peak wherein FWHM and sodium titanate crystallinity are inversely related;

Figure 9 is a plot of the internal temperature in a reactor vs. time during sodium titanate

hydrothermal treatment;

Figures 10A, 10B, 10C, and 10D are scanning electron micrographs (SEM) of each hydrothermally treated pilot plant batch of partially crystalline layered sodium titanate prepared in Example 5 magnified 3000 times;

5 Figure 11 is a plot of the concentration of strontium in the effluent of a partially crystalline layered sodium titanate packed column over time before and after regeneration of the sodium titanate ion exchange material; and

Figure 12 is a plot of the kinetics of strontium uptake by bound and unbound partially crystalline layered sodium titanate of this invention.

DESCRIPTION OF THE CURRENT EMBODIMENT

The present invention relates to a partially crystalline layered sodium titanate having a d-spacing of from about 8 to about 9.9 angstroms, and a 001 reflection peak half width of from 1° to about 4.5°. The new partially crystalline sodium titanate has strong ion exchange properties towards strontium as a result of physical properties that distinguish the composition from all other sodium titanates.

The partially crystalline layered sodium titanate of this invention has the formula $\text{Na}_{3.4} \cdot \text{Ti}_{8.4-9.2} \text{O}_{18.5-20.6} \cdot x\text{H}_2\text{O}$. It is preferred that the partially crystalline layered sodium titanate has the formula $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$.

The non-crystalline layered sodium titanate of this invention also comprises amorphous sodium titanate. As will be discussed below, the combination of the layered partially crystalline sodium titanate and amorphous sodium titanate is the result of hydrothermally treating sodium titanate gel at specified conditions. The resulting partially crystalline layered sodium titanate has a unique X-ray diffraction pattern as well as other unique physical and performance characteristics.

The partially crystalline layered sodium titanate of this invention has been formulated to maximize its strontium ion exchange capacity and selectivity. The strontium ion-exchange property has been deliberately manufactured into the sodium titanate of this invention by controlling the sodium titanate hydrothermal treatment step to produce a sodium titanate product that it is partially crystalline. The hydrothermal treatment variables that affect the crystallinity of the sodium titanate product and, thereby, its strontium ion-exchange capacity and selectivity

are, hydrothermal treatment temperature, the time of treatment, and the concentration of sodium hydroxide used in the hydrothermal treating solution. An additional advantage of the hydrothermal treatment is that it renders the sodium titanate essentially insoluble in strongly alkaline solutions.

- 5 Various methods are used to prepare a sodium titanate gel for hydrothermal treatment. Two methods: the reflux method; and the sol-gel method are described in more detail in the examples. The method used to prepare sodium titanate gel does not significantly affect the strontium ion-exchange properties of the final sodium titanate product.

Strontium ion-exchange affinity is measured by the strontium distribution coefficient, K_d .

- 10 The distribution coefficient, K_d is calculated using the following equation:

$$K_d = \frac{(C_i - C_f)}{C_f} \times \frac{V}{W}$$

- where C_i and C_f are the initial and final solution concentrations of strontium or any other solution ion being tested, V is the volume of the starting test solution, and W is the weight of the sample tested. K_d is typically reported in units of mL/g. The strontium K_d is determined by
15 contacting a known sample of sodium titanate with a solution of known strontium concentration for a controlled period of time, preferably 24 hours. Strontium K_d is solution specific and for most K_d 's reported herein, a solution consisting of 5M NaNO₃/0.1M NaOH/55ppm Sr was used. If a reported K_d is derived from different strontium containing solution, then the solution composition is reported. Strontium K_d is also sample size specific and unless otherwise reported.

each test used 20 mL of solution and 20 mg of solid sample ($V/M = 100 \text{ mL/g}$).

We have discovered that the strontium K_d of sodium titanate is a function of sodium titanate crystallinity. If the sodium titanate product is too crystalline, mass transfer into the sodium titanate will be slowed thereby lowering the strontium K_d . Likewise, if the sodium titanate is not crystalline enough, the sodium titanate will not have the requisite d-spacing to be a good strontium exchanger and the strontium K_d will be low. Thus the sodium titanate of this invention is characterized as "partially crystalline" -- the crystallinity of the sodium titanate of this invention is tailored during the hydrothermal treatment step to control d-spacing and other physical properties, thereby maximizing the strontium K_d of the partially crystalline sodium titanate composition.

At least three physical properties are characteristic of a partially crystalline layered sodium titanate composition of this invention with the required crystallinity to be a good strontium ion exchanger. The properties are, strontium K_d , X-ray diffraction d-spacing, and the 001 reflection peak half width. The latter two properties are derived from the X-ray diffraction pattern of the partially crystalline layered sodium titanate composition of this invention.

The relationship between d-spacing and the X-ray angle of reflection is set forth in Bragg's Law:

$$2d\sin\theta = n\lambda$$

Where d is the d-spacing in angstroms, n is an integer, λ is the X-ray wavelength in angstroms and θ is the X-ray angle of reflection in degrees. The Bragg's Law Equation is a useful tool for interpreting X-ray diffraction patterns since the X-ray diffraction pattern is a trace of 2θ .

The spacing between the sodium titanate layers is ascertained from the x-ray diffraction pattern using Bragg's Law and is known as d-spacing. Sodium titanate is composed of layers of titanium and oxygen atoms separated by voids containing sodium ions and water. The d-spacing is the distance from one titanium or oxygen atom to the identical atom one crystal layer away. D-spacing is the thickness of one titanate layer and one void space. For optimum strontium ion exchange capacity, the sodium titanate of this invention must have a d-spacing of from 8 to 9.9 angstroms, and preferably a d-spacing of from about 9.0 to about 9.9 angstroms. A sodium titanate having the requisite d-spacing admits hydrated strontium, excludes hydrated sodium, and exhibits strontium K_d s in excess of 20,000 mL/g.

Our discovery of a sodium titanate having an optimum crystallinity for strontium ion-exchange derived from our efforts to understand how hydrothermal re-treatment of sodium titanate gels affects the crystallinity of the partially crystalline sodium titanate product. This led to our discovery that sodium nonatitanate has an optimum crystallinity for use as a strontium ion exchanger. The optimum crystallinity can be quantified by measuring the width of the 001 reflection peak at half of it's height (FWHM, units=degrees). The FWHM is inversely proportional to the crystallinity of the sodium titanate material meaning the greater the FWHM, the less crystalline the material is. High strontium K_d 's are obtained when the FWHM is greater than 1 degrees and less than about 4.5 degrees: $1.0 \text{ degrees} < \text{FWHM} < 4.5 \text{ degrees}$, and most preferably when the FWHM is greater than 2 degrees and less than about 4.5 degrees: $2.0 \text{ degrees} < \text{FWHM} < 4.5 \text{ degrees}$.

The layered structure of partially crystalline sodium titanate of this invention is the source

of its ability to selectively exchange strontium. The partially crystalline sodium titanate composition contains spaces between the layers that are large enough to accept hydrated strontium ions. The layer spacing is small enough, however, to exclude hydrated sodium and this prevents hydrated sodium from competing for ion-exchange sites with hydrated strontium.

5 Sodium titanate surface area is related to the rate at which an ion exchanges. The larger the surface area, the faster the strontium exchange rate. Typically, the greater the crystallinity of sodium nonatitanate the lower its surface area is. Thus, there is also a fine balance between crystallinity and exchange rate. A partially crystalline sodium titanate of this invention will have a surface area of from 25-200 m²/g. It is preferred, however, that the partially crystalline
10 sodium titanate of this invention has a surface area of from 60 to 110 m²/g.

Partially crystalline layered sodium titanates of this invention can be prepared by at least two techniques; by the sol-gel technique, and by the reflux technique. Both techniques produce a sodium titanate gel that must undergo hydrothermal treatment which crystallizes at least a portion of the sodium titanate gel to give a partially crystalline layered sodium titanate of this
15 invention. It is the parameters of the hydrothermal treatment parameters, including the NaOH concentration, that are important for producing a partially crystalline sodium titanate composition that has the desired K_d, d-spacing, and FWHM properties.

The sol-gel method for preparing a sodium titanate gel comprises combining titanium isopropoxide and methanol at a weight ratio of from 1:1 to about 1:100 to form a first reaction
20 mixture. A second reaction mixture is prepared by combining NaOH and methanol in a weight ratio that allows the sodium hydroxide to dissolve completely in the methanol. The first reaction

mixture is added to the second mixture to form an admixture and a third reaction mixture comprising water and methanol slowly added to the admixture to initiate gel formation. The final mixture is allowed to gel for a period of time ranging from about 15 minutes to about 2 hours or more. Preferably, the reactor is sealed and agitated at a high rate for a period of time of 30 minutes or longer to keep the sodium titanate gel fluid. The solvent and byproducts are then evaporated from the sodium titanate gel in a vacuum oven operated at from 40°C to about 80°C for a period of time ranging from about 2 hours to about 24 hours or more until most of the methanol solvent and reaction byproduct, isopropanol, is volatilized from the sodium titanate gel.

An alternative and preferred method for producing sodium titanate gel is the reflux method. The reflux method does not use methanol and only produces the corresponding isopropanol byproduct thereby reducing the amount of volatile fumes and wastes produced by the sodium titanate gel formation process as well as making solvent recovery easier and more energy efficient. The reflux process comprises first preparing a solution of sodium hydroxide by dissolving sodium hydroxide pellets in deionized water to give a first solution consisting of from about 10 molar to about 19.2 molar NaOH. Neat -- 99% -- titanium isopropoxide (TiP) is then added slowly to the first solution until the mole ratio of Ti to Na in the mixture ranges from 1:1 to 1:10, and preferably from 1:5 to 1:9. The sodium hydroxide/titanium isopropoxide mixture is then refluxed for a period of time ranging from about 60 minutes to about 4 hours or more at a temperature of from 100-150°C to form an amorphous sodium titanate gel.

The sodium titanate gel produced by either method must be hydrothermally treated in

order to produce the partially crystalline layered sodium titanate of this invention. The hydrothermal treatment is accomplished in a reactor at a pressure ranging from about 45 to about 1000 psig and at a temperature ranging from about 100 to about 250° C. The sodium titanate gel is hydrothermally treated for a period of time ranging from about 1 hour to about 1 day or more.

As the hydrothermal treatment occurs, the autogenous pressure in the reactor vessel increases with increasing temperature. Therefore, the preferred average reactor pressure during hydrothermal treatment ranges from about 50 psig to about 350 psig depending on reaction temperature. The hydrothermal treatment may occur under alkaline conditions created by adding water or a sodium hydroxide solution to the sodium titanate gel before or after it is added to the hydrothermal treatment reactor or autoclave. The hydrothermal treatment step may be repeated at least once in order to increase the crystallinity of the partially crystalline sodium titanate.

To obtain a partially crystalline layered sodium titanate product that falls within the scope of this invention, the hydrothermal treatment step is preferably conducted for 1 to about 20 hours at 160-200°C. By reducing the temperature of the hydrothermal treatment from 200°C to 160°C, the autogenous pressure is reduced from 247 to 90 psia, thereby making the process safer and requiring less expensive equipment. The time reduction from 20 hours to 5 greatly increases the overall productivity of the process.

In some instances, a partially crystalline sodium titanate will not be crystalline enough to have the physical properties of a partially crystalline layered sodium titanate of this invention. In this situation, the partially crystalline sodium titanate can be hydrothermally treated a second

and possibly subsequent times at the conditions recited above in order to increase the crystallinity of the partially crystalline sodium titanate to the desired level.

Table 1, below, shows that the strontium K_d of a partially crystalline layered sodium titanate can be improved in some cases by a second hydrothermal treatment. By closely controlling the hydrothermal treatment step parameter, we can obtain the optimal crystallinity for strontium uptake using one, two, or more hydrothermal treatment steps.

TABLE 1

Table 1. The Effect of Two Hydrothermal Treatments on the Strontium K_d of Sodium Titanate*			
1 st Hydrothermal Treatment	2 nd Hydrothermal Treatment		K_d at 24 hours mL/g
	Temperature °C	NaOH M	
200°C/Water	—	—	48,700
200°C/Water	240	0	75,400
200°C/Water	240	1	127,600

* All hydrothermally treated for 20 hours

The partially crystalline layered sodium titanate of this invention has the formula $\text{Na}_{3.4-4.4}\text{Ti}_{8.4-9.2}\text{O}_{18.5-20.6}$. The partially crystalline sodium titanate is removed from the reactor and washed with deionized water and filtered. The washed product is dried at a temperature from about 50°C to about 100°C for a period of time ranging from about 3 hours to about 2 days or more.

The amount of sodium hydroxide added to the sodium titanate gel can be a critical hydrothermal treatment parameters and must be closely controlled in order to produce a sodium titanate having an optimum crystallinity for strontium ion exchange. In order to manufacture a partially crystalline sodium titanate having a d-spacing of from about 8 to about 9.9 angstroms and a 001 reflection peak half-width greater than 1° and less than about 4.5° , the amount of sodium hydroxide added to the sodium titanate gel during hydrothermal treatment should range from about 0.0M to about 6M, and preferably from 0.50M to about 1.5M. The sodium titanate gel inherently is naturally contaminated with NaOH. So sodium hydroxide will become dissolved in any water added to the sodium titanate gel during gel hydrothermal treatment. It is preferred, however, that an aqueous solution of NaOH in the molarity ranges given above be added to the sodium titanate gel prior to hydrolysis.

The optimum hydrothermal treatment temperature is from about 100°C to about 250°C and preferably from 160 - 200°C . Finally, it is preferred that the strontium K_α of the resulting partially crystalline sodium titanate is at least 20,000 mL/g based on 20mL of solution consisting of 55 ppm Sr/5M NaNO_3 /0.1M NaOH added to 200 mg of solid sample.

The partially crystalline sodium titanate of this invention is very useful when used as an ion exchanger. In order to use the powdered partially crystalline sodium titanate as an ion exchanger, it must be bound into larger particles to reduce the pressure drop in the ion exchange column and to ease handling. Any binder known in the art for binding catalysts and ion-exchangers may be used. However, the bound sodium titanate of this invention is very useful in removing strontium and other radioactive waste from highly caustic aqueous solutions. So,

it is preferred that the binder be selected from materials that withstand radiation and alkaline conditions, and the material should not inhibit or block strontium or other ions from entering the partially crystalline layered sodium titanate. A composite material made up from 40 to 95 wt% of partially crystalline sodium titanate with 5-60 wt% of a binder is preferred.

- 5 Both organic and inorganic binders can be mixed with partially crystalline sodium titanate to make a bound ion exchange composition for strontium. For applications with nuclear waste, inorganic binders offer the advantage of increased radiation resistance. For other applications, organic binders may be easier to extrude into pellets than inorganics.

- 10 Examples of inorganic binders include silica or silica gel, silicon carbide, clays, and silicates, including synthetically prepared and naturally occurring ones, which may or may not be acid treated, for example, attapulugus clay, china clay, diatomaceous earth, fuller's earth, kaolin, kieselguhr, etc.; ceramics, porcelain, crushed firebrick, bauxite; refractory inorganic oxides such as alumina, titanium dioxide, zirconium dioxide, chromium oxide, beryllium oxide, vanadium oxide, cerium oxide, hafnium oxide, zinc oxide, magnesia, boria, thoria, silica-
15 alumina, silica-magnesia, chromia-alumina, alumina-boria, silica-zirconia, etc.; crystalline zeolitic aluminosilicates such as naturally occurring or synthetically prepared mordenite and/or faujasite, for example, either in the hydrogen form or in a form which has been exchanged with metal cations; spinels such as $MgAl_2O_4$, $AnAl_2O_4$, $CaAl_2O_4$, and other like compounds; and combinations of materials from one or more of these groups.

- 20 Other examples of inorganic binders include various metal salts in powder, sol, or gel form, as well as graphite and hydraulic cement may be used to bind any type of sodium titanate.

In addition, Ciment Fondo XR calcium aluminate, and Portland type 3 cement are good sodium titanate binders with excellent strength and resistance to high alkalinity. When cements are used as binders, the bound sodium titanate can be in the form of pellets, can be fashioned with dies, or extruded.

5 Organic binders may also be used to bind partially crystalline sodium titanate. Examples of organic binders include polymers, starches, cellulose, cellulose acetate and other organic catalyst and ion-exchanger binders known in the art.

 Pore formers, surface area enhancers and other materials may be added to the partially crystalline sodium titanate before, during, or after binding to improve the porosity and surface
10 area of the bound crystalline sodium titanate. A preferred pore former is one which can be removed from the ion-exchanger chemically, or thermally before the bound material is used as an ion-exchanger.

 A preferred binder is a hydrolyzable titanium compound. The hydrolyzable titanium compound is useful for binding any form of crystalline titanates including crystalline sodium
15 titanates, crystalline hydrogen titanates, and the preferred partially crystalline sodium titanate. A hydrolyzable titanium compound of this invention will have the formula $Ti XX_1X_2X_3$ wherein X is any constituent, and X_1 , X_2 , and X_3 are each chosen from the group consisting of Cl, Br, I, or OR where R is any acyl or alkyl group containing 10 carbons and wherein R may make one or two points of contact with Ti and oxygen.

20 Preferred hydrolyzable titanium compounds include titanium alkoxides and especially titanium isopropoxide. The hydrolyzable titanium compound is preferably used to bind a form

of crystalline sodium titanate that is a good strontium ion exchanger because the resulting titania binder has little detrimental impact on the strontium K_α of the bound product. A preferred crystalline sodium titanate is a partially crystalline sodium titanate having the formula: $\text{Na}_{3.4-4.4}\text{Ti}_{8.4-9.2}\text{O}_{18.5-20.6}$, a d-spacing of from 8.0 to 9.9, and a (001) reflection peak half-width greater than 1° and less than about 4.5° .

The hydrolyzable titanium compound, preferably titanium isopropoxide, and a crystalline sodium titanate are combined and water from the air and from the crystalline sodium titanate slowly hydrolyze the hydrolyzable titanium compound to form a titania bound crystalline sodium titanate.

The titania bound crystalline sodium titanate may be bound in the presence of an alcohol such as methanol in which case the solid should be dried before use or before further processing. The titania bound crystalline sodium titanate may be dried at ambient conditions or it may be dried in an oven. In a preferred method, the titania bound crystalline sodium titanate is dried in an oven at a temperature of from 75°C to about 100°C for a period of time ranging from about 1 hour to about 12 hours or more.

The dried titania bound crystalline sodium titanate can be used as is, it can be ground and sieved into smaller particles for use as an ion exchanger, or it can be processed further to improve its mechanical properties. It is preferred that the dried titania bound crystalline sodium titanate is further processed first by compaction, and then by calcination. The dried titania bound crystalline sodium titanate can be compacted as produced, or it can be ground into small particles, or into a powder and then compacted. It is preferred that the dried titania bound

crystalline sodium titanate is ground into smaller particles that can be easily compacted.

The titania bound crystalline sodium titanate may be compacted in any powder compaction equipment known such as molding presses, tableting presses, and extruders. Molding presses comprise a mechanically or hydraulically operated press and a two part mold
5 attached to the platens of the press, consisting of top (male) and bottom (female) portions. The action of pressure and heat cause a particulate charge to flow and take the shape of the cavity of the mold.

Tableting presses produce simpler shapes at higher production rates than do molding presses. A single-punch press is one that will take one station of tools consisting of an upper
10 punch, a lower punch, and a die. A rotary press employs a rotating round die table with multiple stations of punches and dies. Older rotary machines are single-sided; that is, there is one fill station and one compression station to produce one tablet per station at every revolution of the rotary head. Modern high-speed rotary presses are double-sided; that is, there are two feed and compression stations to produce two tablets per station at every revolution of the rotary
15 head.

The titania bound crystalline sodium titanate may be dry granulated. In dry granulation, the blended dry ingredients are first densified in a heavy-duty rotary tableting press which produces pellets. The pellets are subsequently crushed into particles of the size required for ion exchange. Densification can also be accomplished using a rotary compactor-granulator system.
20 A third technique, direct compaction, uses sophisticated devices to feed the blended dry ingredients directly to a high-speed rotary press.

Roll presses can also be used to tablet the titania bound crystalline sodium titanate by directing a powder feed into a gap between two rolls rotating at equal speeds. The size and shape of the compacted pellets are determined by the geometry of the roll surfaces. Pockets or indentations in the roll surfaces form briquettes from a few grams up to 5 lb. or more in weight. Smooth or corrugated rolls produce a solid sheet which can be granulated in the desired particle size on conventional grinding equipment.

Lubricants added to the powder feed can aid in the transmission of compaction forces and reduce sticking to the die surfaces. Lubricants that are removed from the bound material at calcining temperatures may be incorporated into the titania bound crystalline sodium titanate prior to compaction. Such lubricants may be selected from the group comprising boric acid, graphite, oils, soaps, starch, stearic acid, and waxes. A preferred lubricant is stearic acid and it is preferably present in the powder compactor feed in an amount ranging from about 0.1 to 4.0 weight percent.

The compaction step should produce a compact particle or pellet having a piece density ranging from about 1.5 to about 2.5 g/ml. It is most preferred that the compressed titania bound crystalline sodium titanate particle has a piece density ranging from 1.8 to 2.2 g/ml.

The compacted titania bound crystalline sodium titanate particles are calcined at a temperature ranging from about 150°C to about 500°C for a period of time ranging from 30 minutes to 10 hours or more. It is preferred that the particles are calcined in air at a temperature of from about 200°C to about 400°C for a period of time ranging from about 30 minutes to about 5 hours. It is most preferred that the particles are calcined in moist air at the

conditions identified above.

Bound and unbound sodium titanate ion exchangers are useful in removing strontium and other radioactive and non-radioactive metals from aqueous solutions by packing bound or unbound sodium titanate into a column and removing target metals from the aqueous streams which are fed in to the column. Using this configuration, crystalline sodium titanate can remove metals from large volumes of aqueous solutions. Sodium titanate ion-exchangers can also be regenerated with an acid, and reused without loss of performance. Furthermore, bound crystalline sodium titanate is able to remove strontium from aqueous streams having a pH of at least 9.95 up to 13 or more, and a Na ion molarity of from about 1.0 to about 5.0 or more without significant loss of exchanger capacity or physical integrity.

When used in processing nuclear waste, the ion-exchange columns should be made out of glass, and may be lined with a polymer for caustic protection. Once the exchanger is spent, the sodium titanate, along with the glass column can be vitrified to act as a impervious barrier for the radioactive strontium.

The unbound and bound sodium titanate of this invention is useful as an ion exchanger for metals besides strontium. Specifically, the sodium titanate is useful, either alone or bound, in removing actinides, and especially uranium, from aqueous solutions. Other actinides which can be similarly removed include thorium, plutonium and americium.

Sodium titanate may be used as an ion-exchanger as produced or it may be converted into H-titanate and used as an ion-exchanger for metals such as ytterbium, zirconium, molybdenum, silver, thallium, lead, chromium, vanadium, iron, cesium, tin, arsenic, and other metal ions with

a high affinity towards hydrogen titanate.

The sodium titanate of this invention is also useful either alone or with a binder, to exchange a wide variety of metals at alkaline conditions. The metals are ranked according to uptake in Table 2 below. For example, lithium, magnesium, nickel, cobalt, and barium are
5 exchanged by a partially crystalline sodium titanate in amounts equal to or greater than strontium. Among the priority pollutants, partially crystalline sodium titanate has a high affinity for zinc, copper, cadmium, mercury, thallium, and lead. Among the precious metals tested, silver has a very high uptake by sodium titanate. As seen in Table 2, these results indicate that sodium titanate can be used to remove metals from industrial effluent and other aqueous metal
10 containing waste, as well as recover target materials.

The ion exchange results reported in Table 2 are based on batch tests using 200 mg sodium titanate, (sample 5-1 from Example 5, *infra*) an aqueous 20 mL solution containing 20 ppm of the metal ions being screened, at alkaline conditions (pH 10-11). Sodium was present in all samples, and the results reflect high selectivities for the indicated metals over sodium.
15 Sodium titanate is useful only as a cation exchanger, and therefore it did a poor job exchanging some metals, including As, Sb, Mo, and Pb at high pH.

TABLE 2

Metals Affinity for Sodium Titanate. Conditions: initial metal ~20 ppm, final pH 9.95-11.14.

	Target Metal	K _a mL/g	Industries where metal is present in effluent
5	Lithium	> 19900	Nuclear, Military
	Magnesium	14900	Mining Paint
	Nickel (II)	> 7400	Electroplating, Explosives, Foundry, Wood, Tanning, Mining, Paint, Petroleum, Enameling, Paper, Textiles
	Cobalt (II)	6900	Mining, Paint, Enameling
10	Barium	6570	Paint
	Strontium	6570	Mining, Nuclear
	Zinc	5570	Electroplating, Explosives, Foundry, Wood, Tanning, Mining, Paint, Enameling, Paper, Textiles
15	Silver	5150	Electroplating, Explosives, Foundry, Wood, Mining, Paint, Petroleum, Textiles
	Copper (II)	2900	Electroplating, Explosives, Foundry, Wood, Tanning, Mining, Paint, Petroleum, Enameling, Paper, Textiles
20	Cadmium	2120	Electroplating, Foundry, Wood, Mining, Paint, Petroleum, Enameling, Textiles
	Calcium	1900	Mining, Paint
	Mercury (II)	> 1800	Foundry, Wood, Mining, Paint, Petroleum, Enameling, Paper, Textiles
25	Thallium (I)	> 1800	wood, Mining, Paint, Petroleum, Textiles
	Lead (II)	1700	Electroplating, Explosives, Foundry, Wood, Tanning, Paint, Petroleum, Enameling, Paper, Textiles
	Ytterbium (III)	1400	Nuclear
	Manganese (II)	1030	Mining, Paint, Enameling
30	Rubidium	658	Nuclear
	Cesium **	492	Nuclear
	Tin (II)	217	Electroplating, Paint, Enameling
	Chromium (III)	92	Electroplating, Foundry, Wood, Tanning, Mining, Paint, Petroleum, Enameling, Paper, Textiles
35	Antimony (V)	87	Explosives, Foundry, Wood, Mining, Paint, Petroleum, Enameling, Textiles
	Aluminum	69	Mining, Paint, Enameling
	Vanadium (V)	33	Mining, Paint
40	Iron (III)	33	Electroplating, Mining, Paint, Enameling
	Zirconium	17	
	Arsenic (V)	0	Foundry, Wood, Mining, Paint, Petroleum Enameling, Textiles
	Molybdenum (VI)	0	Mining, Paint, Enameling

45 ** Initial [CS] = 43 ppm

EXAMPLE 1

This Example describes a reflux method for manufacturing sodium titanate gel of this invention followed by hydrothermal treatment to produce a partially crystalline sodium titanate.

5.85 g of NaOH pellets were dissolved in 14 mL of distilled deionized water (DDI). 32
5 mL of titanium isopropoxide (TiP) was then added slowly to the NaOH solution. This mixture
was then refluxed for 3 hrs at which time it was then transferred into a Teflon lined bomb using
distilled deionized water (except for Sample 1-2 which used 20 mL of 0.82 M NaOH solution).
The bomb was sealed and placed in a 190°C oven and allowed to react for 20 hrs. The material
was collected by filtration and washed one time with DDI and three times with methanol. The
10 initial Ti concentration in the bomb was 1.58 M and the initial concentration of NaOH in the
bomb was 2.46 M. The Ti:Na ratio was 1:1.56.

Table 3 lists the properties of partially crystalline sodium titanates prepared by the
method of this Example. The solution used to derive the strontium K_d data included 5M NaNO_3 ,
0.1M NaOH and 90-95 ppm Sr^{2+} . The solution to sample weight ratio was 200:1 unless
15 otherwise reported.

TABLE 3

Sodium Titanates Prepared by Method of Example I

Sample	Ti M	NaOH M	Ti : Na Mole ratio	Reflux time (hrs)	Hydrothermal Temp. (time)	Sr K ^d (mL/g)
1-1	1.1	1.5	1:1.37	3.25	200 (20 h)	3,180
1-2	1.6	2.5	1:1.56	3	190 (20 h)	11,800*
1-3	1.0	2.0	1:2	3	200 (20 h)	5,340
1-4	1.0	4.0	1:4	3	200 (20 h)	19,900
1-5	0.63	3.1	1:5	2	170 (22.5 h)	≥95,000
1-6	0.65	4.5	1:6.9	3.2	193 (19.7 h)	≥95,000
1-7	0.58	5.1	1:8.9	3.2	193 (19.7 h)	≥95,000
1-8	0.90	9.0	1:10	3.2	190 (21 h)	---
1-9	0.44	8.35	1:19.4	16.5	200 (1 d)	---
1-10	0.75	5.1	1:6.8	1 hr	200 (4 d)	42,800
1-11	0.43	0.87	1:2	3.5	145 (4 d)	692**
1-12	0.69	1.4	1:2.1	3	200 (7 d)	710**
1-13	gel	gel	1:1.37	NA	200 (1 d)	3,360*

* The solution to sample v/w ratio was 250:1.

** The solution to sample v/w ratio was 400:1.

The XRD patterns of samples 1-1 to 1-13 are shown in Figures 2 and 3. Samples 1-6, 1-7, and 1-10 each have d-spacing below 9.9 and greater than 8.0 and 001 reflection FWHM's of between 1° and 4.5°.

EXAMPLE 2

This Example describes a method for preparing a sodium titanate designated as sample 2-1 by subjecting sample 1-2 of Example 1 to a second hydrothermal treatment. 3.50 g of sample 1-2 was placed into a Teflon lined bomb. 38 mL of 4.2 M NaOH solution was added to the solid. This mixture was then treated hydrothermally for 2 days at 170°C. The sample was collected by filtration and washed one time with DDI, four times with methanol, and two times with ethanol. The X-ray diffraction pattern of sample 2-1 is found in Figure 4.

As seen in Table 5, the K_d before the second hydrothermal treatment (sample 1-5) was 3,060 mL/g and after the additional hydrothermal treatment (sample 2-1), 1270 mL/g.

10

EXAMPLE 3

This example details the preparation of a partially crystalline layered sodium titanate of this invention by the sol-gel method.

Solution B was made in a plastic beaker by dissolving 40.793 g of 98.4 % NaOH pellets
5 in 400 mL of methanol. The NaOH is not readily soluble in methanol. Therefore, the mixture was stirred for over 30 minutes with a magnetic stirrer.

Solution A was made by mixing 294.2 g of titanium isopropoxide (TiP) and 250 mL of methanol in the reaction vessel. The heat of mixing is exothermic (the temperature reached 72° C). The reaction vessel was a 2-liter glass beaker wrapped with insulation tape. Next, solution
10 B was slowly added to solution A in the reaction vessel. The contents were stirred with a magnetic stirrer, and heated to 53°C on a hot plate.

Solution C was made in a 100 mL beaker by mixing 20 mL water and 50 mL methanol. Using a buret, solution C was added drop-wise to the heated mixture of A and B (53°C). The resulting sodium titanate gel was mixed for another 15 minutes, then transferred to a ceramic
15 evaporating dish. The solvents were allowed to evaporate overnight in a hood. Next, about half the gel was loaded into a liter round bottom flask, which was then connected to a rotary evaporator. The gel was dried under vacuum for 1.5 hours at 60-75° C. The rotary evaporation procedure was repeated for the second batch. This procedure yielded 135 g of dried gel.

To make the final sodium titanate product, 20 g of the precursor gel was mixed with
20 either 40 mL of deionized water, or 40 mL of 1 M NaOH in a Teflon lined Parr autoclave. The contents were then hydrothermally treated at 160-200°C for 5-20 hours.

EXAMPLE 4

This example details the preparation of a partially crystalline sodium titanate of this invention using the reflux method followed by hydrothermal treatment.

5 A 30% NaOH solution was prepared by dissolving 419.88 g of 98.4% NaOH pellets in 956 g of deionized water. This solution was transferred into a 3000 mL, 3-necked round bottom reaction flask. 295.3 g of titanium isopropoxide (TiP) was added drop-wise from a 500 mL addition funnel into the NaOH solution in the reaction flask. During the addition, the mixture was stirred at 500 rpm. A large amount of white solids precipitated out of solution.

10 The reaction vessel was placed on a heating mantle, and equipped with a condenser, thermocouple and temperature controller, and mixer. The mixture was stirred at 250 rpm and refluxed at 110° C for 5.25 hours. The sodium titanate gel product was allowed to cool and settle out overnight. The water was then decanted, and the solids dried at 60°C for 2 days. The yield was 152 g of sodium titanate gel.

15 To make the final product, 20 g of the precursor was mixed with either 40 mL of deionized water, or 40 mL of 1 M NaOH in the Teflon lined Parr autoclave. The contents were then hydrothermally treated at 160-200°C for 5-20 hours.

EXAMPLE 5

10 kg of sodium titanate gel were made using the sol gel method according to this example. A 50 gallon reactor was charged with 30 kg titanium isopropoxide and 20.6 kg methanol. To this mixture, a solution of 4.2 kg NaOH and 32.8 kg methanol was slowly added
5 from one of several 20 gallon mixing tanks. A 2.1 kg water/4.1 kg methanol solution was then slowly added to initiate gel formation. Methanol evaporation from the reactor was eliminated by applying pressure, and high agitation rate, (681 ft/min), to keep the gel fluid. This meant that after a gelation period of 30 minutes, the gel flowed freely from the reactor. The gel was emptied onto trays which were placed in a 60°C vacuum oven at 27 in. Hg for 12 hours.
10 Methanol solvent (about 56 kg), and byproduct isopropanol (about 21 kg) were evaporated from the product in the oven.

The dried gel was divided into four batches and treated hydrothermally in a 5 gallon stainless steel-lined autoclave. The autoclave liner was capped with a sheet of Teflon. Table 4, below, summarizes the conditions of each hydrothermal treatment. For each of batches 5-1
15 and 5-2, 4.5 kg of dry gel was hydrothermally treated in 9 kg of water for 20 hours at 160-200°C. For batches 5-3 and 5-4, 2.6 kg of dry gel was treated in 5.2 kg of water for 5 hours at 160-200°C. All non-stirred batches formed a solid chunk by the end of the autoclave step. This solid was easily dispersable in water. Batch 5-4 was agitated throughout the treatment. The material from batch 5-4 was a finely suspended slurry, and therefore was very easy to remove
20 from the autoclave.

The top layer of water on each batch in the autoclave was suctioned off and the

remaining solid slurry was transferred to a filter bag within a centrifuge. 7 kg of deionized water was used to wash the solids clinging to the sides of the autoclave. The solids were centrifuged for 10 minutes to remove the water. An additional 4 kg of water was added to the solids and then centrifuged to wash the product. The product was dried overnight in a 65°C oven with a flowing nitrogen purge. The combined yield of all four batches was 9.2 kg of partially crystalline sodium titanate.

TABLE 4

Batch	Time (hr)		Internal Temperature ° C **		Internal Pressure (psig)		Mixer	Dried Gel Charged (kg)	Yield of Final Product (kg)
	Heat Up & Cool Down	At Temp *	high	Ave	Range	Ave			
5-1	26	20	200	200	140-310	275	off	4.50	2.37
5-2	20	20	200	198	190-305	285	off	4.50	3.98
5-3	15	5	200	199	155-330	300	off	2.60	1.61
5-4	13	5	210	205	150-372	350	on	2.60	1.23

* At time = at temperature between 160-200° C

** Internal temperature high and average during when the autoclave was at temperature.

EXAMPLE 6

X-ray powder diffraction (XRD) patterns of the synthesized materials from Examples 1 and 2 were prepared and the results are shown in Figures 1-3. The XRD patterns indicate, for the reflux samples, that as the mole ratio of Na/Ti increases, the crystallinity of the titanate material also increases until a ratio of 5 is reached. At this ratio, what appears to be a less crystalline compound, forms.

The most crystalline samples 1-8 and 1-9 were made with the highest ratios of NaOH to Ti and in the strongest base solutions. The X-ray pattern for sample 2-1 shows that this twice hydrothermally treated sample is more crystalline than its precursor 1-2. Samples 2-1, 1-8 and 1-9 exhibited K_d values that were considerably lower than those of the less crystalline samples. For example, sample 1-8 had a strontium K_d of 7000 mL/g in 0.1M NaNO_3 . Under the same conditions, sample 1-1 had strontium K_d value in excess of 100,000 mL/g.

Examination of the X-ray patterns leads to a conclusion that different types of materials have been made. A more crystalline variety which appears to resemble sample 2-1 are samples 1-1, 1-2, 1-3, and 1-5 and a more gel-like group as exemplified by 1-6, 1-7, and 1-10, and a sample of intermediate crystallinity between the two, sample 1-4. It is sample types 1-10 and 1-7 that provide the highest K_d values.

Sample 1-13 (gel-based) and 1-2 (reflux-based) have similar Na:Ti mole ratios and were reacted for approximately the same time period and temperature, but turn out to be different structure nonatitanates. The X-ray diffraction pattern for the gel sample was similar to the high Na:Ti ratio reaction material 1-10, but has much lower ion exchange selectivity toward Sr^{2+} .

Upon comparing the X-ray diffractions patterns of sample 1-12 and 1-3 it appears that longer hydrothermal treatment does not change the crystallinity of the composition but it does have a definite effect upon its ion exchange properties.

EXAMPLE 7

This Example describes the strontium distribution coefficient (K_d) results titanates prepared in Examples 1 and 2. The distribution coefficient as defined in is the ratio of the concentration Sr^{2+} in the exchanger to the concentration of Sr^{2+} in solution at equilibrium. Because the analyses were carried out on a weight basis, the units are g/g instead of the usual mL/g. The distribution coefficients (K_d) were determined for Sr^{2+} as a function of pH for three of the samples, 1-1, 1-10, and 2-1. The resulting data are shown in Figure 5. As the pH of the solution decreases, the selectivity for Sr decreases. The K_d at pH values above 11 are reported as being greater than 300,000 because at this pH, the Sr concentration was below the detection limit of the AA unit and a value of 0.1 ppm was used to calculate the K_d . It is important to mention that there is typically a large difference between the initial pH of the Sr solutions and equilibrium pH after exchange. This is due to the hydrolysis of the sodium nonatitanate whose reaction is shown below. This property is found in all the layered titanates.

$$\text{Na}_4\text{Ti}_9\text{O}_{20} + x\text{H}_2\text{O} \longrightarrow \text{H}_x\text{Na}_{4-x}\text{Ti}_9\text{O}_{20} + x\text{NaOH}$$

Distribution coefficients for Sr^{2+} were also determined for these same samples in the presence of 5 M NaNO_3 and 1 M NaOH and 90-95 ppm Sr^{2+} with a solution mass:sample mass ratio of 400:1. The results are found in Table 5, below. Sample 1-10 exhibits the best performance under the conditions studied. When examining samples treated for longer hydrothermal periods with that of their X-ray diffraction equivalents (sample 1-12 with sample 1-3), the Sr K_d 's decrease by a factor of 2. This suggests that very short hydrothermal treatment periods will produce highly selective materials.

When reduction of loading was done, a corresponding increase in K_d was observed. For example, the strontium distribution coefficient of sample 1-10 increased to 58,700. The increase in K_d on reduction of the solution volume from 400 mL to 200 mL indicates that the larger volume of solution contains enough strontium ion to exceed the capacity of the exchanger in 6 M Na^+ . We may assume that a K_d of 58,700 g/g represents an uptake of 99% of the added Sr^{2+} . The exchange capacity of $\text{Na}_4\text{Ti}_2\text{O}_7$ is 4.75 meq/g and in the 200g solution the uptake was 0.2 meq/g thus 4.2% of the capacity was utilized in the experiment where solution to solid weight ratio was 400 and the K_d was 13,400 g/g. Calculation shows that 97% of the Sr^{2+} was taken up. Thus, the loading was $2 \times 0.2 \times 0.94 = 0.388$ meq or 8% of the exchange capacity. This figure represents a very high value for such strong solutions with such high sodium concentrations.

TABLE 5

Sample	Initial pH	Final pH	Sr K_d (g/g)
1-10	13.63	13.80	9,780
1-11	13.63	13.82	692
1-12	13.63	13.74	710
1-1	13.63	13.74	1,270
2-1	13.63	13.74	1,270
1-5	13.6	13.8	3,060
1-4	13.6	13.7	1,730

VIM = 400

EXAMPLE 8

A portion of sample 1-6 was placed on a piece of Whatman filter paper and inserted into a longneck round bottom flask which contained distilled deionized water. The flask was gently heated to produce water vapors which would then impregnate the partially crystalline layered sodium titanate sample. A second portion of sample 1-6 was placed in a 75°C oven until needed. For the K_d measurements, TGA, and XRD pattern of this dried material, the second portion of sample 1-6 was removed from the oven and immediately transferred to the appropriate testing container to help prevent absorption of moisture. The K_d measurements were done using a solution containing 5 M NaNO_3 , 1 M NaOH , and 91.67 ppm Sr^{2+} . The results are shown in Table 6 below. From the XRD patterns (Figures 6 and 7), it can be seen that the dehydrated 1-6 sample possessed a d-spacing in the range of 9.0-9.9 Å while the hydrated sample possessed d-spacing in the range of 9.4-10.2 Å. The results, found in Table 6, show an initial average sodium titanate d-spacing less than about 9.9 angstroms plays a considerable role in promoting the uptake of Sr^{2+} and is related to the state of hydration of the initial exchanger.

Table 6 -- Sr K_a's for a hydrated and slightly dehydrated partially crystalline sodium

Sample	Sr K _a (p/g)
1-6 (1) dehydrated	≥ 254,000
5 1-6 (2) dehydrated	229,000
1-6 (1) hydrated	18,600*
1-6 (2) hydrated	21,200*

- 10 * The weight of the sample was adjusted for the excess water which is contained by multiplying by 0.8163 which was determined by TGA data.

EXAMPLE 9

This Example examines the effect of the hydrothermal treatment step on the strontium K_d of a partially crystalline layered sodium titanate. Four parameters were studied: method of gel preparation (sol-gel or reflux), concentration of NaOH in the autoclave, the time, and the temperature of the hydrothermal treatment step.

The source material for the experiments was sodium titanate gel made by the sol-gel method and by the reflux method and made according to Examples 3 and 4. The results in Table 7 indicate that the strontium K_d 's for partially crystalline sodium titanates prepared by hydrothermally treating amorphous sodium titanates are two times greater for material treated at 160°C for 5 hours than at 200°C for 20 hours. The most statistically significant hydrothermal treatment variable affecting the 24 hour K_d data is the relationship between the concentration of NaOH and the temperature during the hydrothermal treatment step. Control of both of these parameters is necessary to fine tune the crystallinity of the final product.

TABLE 7

The Effect of the Hydrothermal Treatment Conditions on the Strontium K_d of Sodium Titanate					
Sample Number	Gel Method	Temperature °C	NaOH M	Time hr	K_d at 24 hours (mL/g)
9-1	sol-gel	160	0	5	22,400
9-2	reflux	160	1	5	35,500
9-3	reflux	160	1	5	35,500
9-4	sol-gel	160	1	20	21,700
9-5	reflux	200	0	5	8,140
9-6	sol-gel	200	1	5	24,100
9-7	sol-gel	200	0	20	10,600
9-8	reflux	200	1	20	21,700
9-9	reflux	200	0	20	6,660

EXAMPLE 10

In this Example, the strontium K_α of partially crystalline sodium titanate prepared in Example 5 was evaluated. Table 8, below, summarizes the hydrothermal treatment conditions and properties of the four batches of sodium titanate prepared in Example 5. Batches 1 and 2, which were hydrothermally treated for the longest period of time, (160-200° C for 20 hours), were the most crystalline, as indicated by the low full width at half maximum of the largest peak in their X-ray pattern. These most crystalline materials also have the lowest K_α 's because high crystallinity hinders the interlayer diffusion, thereby lowering strontium uptake.

TABLE 8

Summary of the Pilot Plant Hydrothermal Treatments					
Batch	Time at Temp. ¹	Mixer	Yield of Final Product kg	Crystallinity FWHM ² deg	Sr K_α ³ mL/g
5-1	20	off	2.37	1.13	12,100 \pm 2,100
5-2	20	off	3.98	1.92	10,200 \pm 420
5-3	5	off	1.61	2.67	19,800 \pm 410
5-4	5	on	1.23	2.23	21,100 \pm 2,310

¹ At temp. = at temperature between 160-200°C.

² FWHM = 001 reflection peak full width at half maximum.

³ 5M NaNO₃/0.1M NaOH/68.6 ppm Sr.

The sodium titanate from all four batches have a high strontium K_d . But the strontium K_d for the batches hydrothermally treated for 5 hours are about two times higher than for the batches treated for 20 hours (20,500 vs. 11,500 mL/g). This difference may be correlated with the degree of crystallinity of the samples. Figure 8 is a plot of the strontium K_d of the batches as a function of FWHM (full width at half maximum peak height of the 001 reflection peak). The larger the FWHM, the less crystalline the material. The materials with the higher crystallinity (batches 1 and 2) have the lower K_d s.

The X-ray pattern for batch 2, shows a major peak at 8.76 angstroms. This peak is still present after stirring the sample with 0.1 M NaOH. By this observation, the new peak is not a $H_4Ti_9O_{20}$ phase (which should result if the sample were washed with too much water in the pilot plant). Batch 2 may contain another sodium titanate phase, possibly $Na_7Ti_3O_7$, which has its major peak at 8.270 angstroms. All other batches contain only nonatitanate. Compared to the other batches, Figure 9 shows that batch 2 has the longest period at the internal temperature of 200°C (18 hours). This extended heating period may have allowed the new phase to form.

Figures 10A, B, C, and D show scanning electron micrographs (SEM) of each of the pilot plant batches at 3000 times magnification. The partially crystalline sodium titanate of batches 1 through 3, Figures 10A, 10B, and 10C, shows the material to have formed nuggets, while batch 4, Figure 10D consists of elongated bundles of fibers. While mixing does not affect the resulting strontium K_d , it does influence the gross morphology of the exchanger. Mixing the gel during hydrothermal treatment causes shear stresses in the newly forming sodium titanate, which in turn results in a higher number of loose fibers and elongated bundles.

EXAMPLE 11

Fondo XR cement (8.6g) and sodium titanate (20g, - 200 Mesh) prepared by the method of Example 5 were dry blended vigorously for 5 minutes to form a bound sodium titanate. Subsequently, deionized H₂O (14.7g) was slowly added while mixing continuously. The mixture
5 was allowed to blend for an additional 5 minutes. The paste like mixture was thinly spread over a Teflon sheet. The sheet was placed in covered pans and exposed to water saturated in an oven at 30°C and cured for 48 hr. The cured sheets were broken down to 20 x 40 mesh size with mortar and pestle.

EXAMPLE 12

This example details a method for preparing an amorphous sodium titanate bound crystalline sodium titanate.

In a beaker located on a magnetically stirred hot plate, 293 g of titanium isopropoxide (TiP) was mixed together with 250 mL of methanol. The solution was heated to 50°C. Next, a solution of 40.7 g NaOH in 400 mL methanol was added to the beaker. To this mixture, 10 g of through 200 mesh sodium titanate prepared by the method of Example 5 was added. After adding a solution of 50 mL methanol and 20 mL water, the solution plus solids mixture was stirred for 1 hour. The resulting thick paste was spread out on a Teflon sheet and air-cured for 6 days. The cured plaque was ground with a mortar and pestle, then sieved to obtain 20-40 mesh particles. The resulting bound ion exchange compound is a semi-crystalline sodium titanate bound with amorphous sodium titanate.

15

EXAMPLE 13

This example details the preferred method for preparing an titania bound partially crystalline sodium titanate.

5 Six grams of sodium titanate, having a particle size that passes through 200 mesh, prepared by the method of Example 5, was mixed with 10 mL of titanium isopropoxide (TiP). The mixture was agitated until it formed a thick paste. The paste was subsequently spread on a Teflon sheet and air-cured for 45 minutes. After air-curing, the plaque was cured in the oven at 85°C overnight. The cured plaque was ground with a mortar and pestle, then sieved to obtain 20-40 mesh particles. The resulting compound is a partially crystalline sodium titanate bound
10 with an amorphous titania.

EXAMPLE 14

Column experiments were carried out on sample 1-2 (sodium nonatitanate) using a model solution in order to examine the performance of the exchanger under dynamic conditions. Composition of the model solutions was as follows: 5 M NaNO₃, 1 M NaOH, 0.15 M KCl, Cs-
5 13.9 ppm, Sr-8.75 ppm and Ca-4.08 ppm. The volume of the absorbent was 0.85 cm³, the absorbent's layer height was 155mm, the absorbent granules size was <0.1 mm, and the flow rate was 3 bed volumes (b.v.) per hour. The regeneration of the exchanger was achieved by passing 15 mL of a 0.5 M HCl solution through the column at a rate of 0.5 b.v./hr and then subsequent treatment with 20 mL of a solution containing 5 M NaOH, and 0.15 M KCl (0.5
10 b.v./hr) to give a regenerated partially crystalline sodium titanate.

The breakthrough curve for Sr sorption is shown in Figure 11. The curve shows that the partially crystalline sodium titanate effectively purifies approximately 700 column volumes, (c.v.), of the model solution in the first sorption cycle, and after regeneration, the material purifies nearly twice the number of c.v.'s (1200) in the second cycle.

15

EXAMPLE 15

Pellets of sodium titanate prepared by the method of Example 5 combined with Portland cement and calcium aluminate (Ciment Fondu) were prepared according to the method of Example 11, based on the recipe set forth in Table 9, below.

5 Sr-K_d measurements for the Fondu and Portland cement at various curing times are found in Table 9 below. The K_d values were taken using standard test conditions. The Sr-K_d values at all curing times are low when compared to Sr-K_d values of 1633 mL/g for the -200 mesh virgin partially crystalline sodium titanate. The Ciment Fondu binder exhibits a slightly higher Sr-K_d than the Portland cement. There was no obvious effect of the curing time on the final
10 properties of the inorganically bound partially crystalline sodium titanates.

TABLE 9
Effect of Curing Time and Cement Composition of Sr-K_d of Bound Sodium Titanate.

Sample ID	Binder Type 50 wt%	Curing Time (days)	Final Sr Concentration (ppm)	Sr-K _d (ml/g)
15-1	Ciment Fondu	4	40.2	136
15-2	*	11	29.9	252
15-3	*	21	31.0	236
15-4	Portland Type III	4	54.1	50
15-5	*	11	55.5	44
20 15-6	*	21	56.4	40

To determine if the sodium titanate was blinded by the inorganic binder, samples were analyzed via nitrogen porosimetry. The results are shown in Table 10 below and indicate that

the inorganic binders have encapsulated some of the sodium titanate powder as shown by the decrease in both the BET and Langmuir surface areas in the bound samples as compared to the sodium titanate powder.

To determine the extent of mass transfer difficulties, Sr-K_d measurements were taken over a period of 120 hours for bound and unbound samples. Figure 12 and Table 10 show that the bound sodium titanate exhibits the fastest uptake of Sr. Both organic and inorganic binders reduced the rate of Sr uptake. The organic binder made with the pore former has a relatively quick Sr uptake and eventually reaches the value of the sodium titanate powder. However, the inorganic binders have very slow Sr uptake and do not asymptotically reach the same concentration as with the sodium titanate powder. As mentioned above, the inorganic binder appeared to blind the sodium titanate powder. Since the final concentration of Sr does not approach the final concentration observed with the sodium titanate powder, a portion of the sodium titanate appears to be totally encapsulated. Cement bound absorbents using only pure cement have both caustic and mechanical stability, but some mass transfer ability is lost as a result of the binder.

TABLE 10
Effect of Inorganic Binder on Pellet on Surface Area

Sample	Langmuir Surface Area (m ² /g)	BET Surface Area (m ² /g)	Average Pore Radius (Å)
Sodium Titanate	106.7	59.9	39.7
Bound with Ciment Fondu	39.3	22.8	43.4
Bound with Portland Type III	52.1	30.0	64.1

EXAMPLE 16

This Example describes methods of introducing porosity into the inorganic binder/ion exchanger system to improve mass transfer. By increasing the porosity of the ion exchanger pellet, mass transfer of cations into the exchanger increases and therefore increases the amount of radioactive cation captured. Two methods investigated for increasing porosity were gas
5 foaming of the binder-exchanger and addition of inert fillers to the binder-exchanger system. The inert filler was leached out to form porous pellets. All samples using pore formers were prepared by using the general procedure listed in Example 15.

In the first method of producing porous pellets, aluminum was added to the mixture to
10 induce gas formation in the binder-exchange system. The aluminum reacts with water under caustic conditions to produce hydrogen. The hydrogen produces bubbles or voids in the pellet. Results are shown in Table 11 for varying loadings of aluminum and particle size. All of the samples passed the standard caustic stability test. Samples 16-1 and 16-2 were subjected to a small normal force by placing a small weight on the sheet. These sheets did not expand to the
15 same extent as the other samples and have slightly lower product yields. The K_d values for all the porous pellets are significantly lower than that seen with the virgin partially crystalline sodium titanate powder which has a K_d value typically greater than 10,000 mL/g.

TABLE 11
Effect of Al as Porosity Modifier on Sr-K_d of Fondu Bound Sodium Titanate.

Sample ID	Binder Wt%	Exchanger Wt%	Aluminum Wt%	Al Size (Micron)	Final Sr Concentration (ppm)	Sr-K _d (ml/g)
16-1	49	49	2	20	29.6	132
16-2	49	49	2	45	19.8	246
16-3	49	49	2	20	48.0	43
16-4	49	49	2	45	46.2	48
16-5	48	48	4	20	30.0	129
16-6	48	48	4	45	29.3	134

One aluminum filled porous sample was sent for surface area determination via nitrogen porosimetry and exhibited a Langmuir surface area of 111.1 m²/g, a BET surface area of 63.2 m²/g, and an average pore radius of 32.2 angstroms. The aluminum filler increased both the BET and Langmuir surface areas in the bound samples to surface areas similar to that seen in the unbound sodium titanate. Even with the increased surface area, the Sr-K_d for this sample was small.

In the second method of producing porous pellets, inorganic or organic fillers were blended and cured with the binder-exchanger system described in Example 11. The inorganic fillers were calcium carbonate and calcium sulfate while the organic filler was a low molecular weight hydrocarbon wax. These fillers have low solubility in water but can be leached out with the appropriate leaching solutions.

TABLE 12
Effect of Inorganic Fillers on Sr K_d of Fondu Bound Sodium Titanate.

Sample ID	Sample	Particle Size (mesh)	Sr K_d (ml/g)
16-7	Sodium Titanate bound with 50% Ciment Fondu (20 vol % extracted wax)	20 x 40	150
16-8	"	-200	112
16-9	Sodium Titanate bound with 50% Ciment Fondu (20 vol % extracted wax)	20 x 40	150
16-10	"	-500	132

Typical results for the two inorganic fillers are shown in Table 12. These samples were each leached with acid and the sodium titanate was regenerated using sodium hydroxide. All of the K_d values of the inorganic salt filler pellets were lower than the K_d of the virgin sodium titanate powder.

Organic pore formers were used to increase porosity without introducing additional calcium to the system. The organic pore formers were added into the system at different volume percent loading as listed in Table 13. There was no increase in K_d as the porosity due to leached wax increased. The strontium K_d did increase with increased exchanger loading for samples 16-13 and 16-14. This was also observed with the inorganic fillers. There appears to be an upper limit to the amount of exchanger that can be added without loss of mechanical strength. The K_d values were again lower than the virgin sodium titanate powder.

TABLE 13
Effect of Organic Fillers on Sr-K_d of Fondu Bound Sodium Titanate.

Sample ID	Binder Wt%	Exchanger Wt%	Filler Type	Filler Wt% (Vol %)	Sr-K _d (ml/g)
16-11	34.6	34.6	Petrolite 185	30.9 (60%)	383
16-12	30.8	46.5	Petrolite 185	22.7 (40%)	524
16-13	36.9	36.9	Petrolite 185	26.3 (50%)	299
16-14	43.0	28.8	Petrolite 185	27.7 (50%)	552
16-15	37.0	37.0	Petrolite 185	26.0 (50%)	372
16-16	37.0	37.0	Petrolite 185	26.0 (50%)	429

EXAMPLE 17

Cement or calcium exchanged bound sodium titanate can be fully regenerated with an acid wash followed by a caustic wash. However, when the acid wash was tested on cement or calcium exchanged, cement bound sodium titanate, the pellet broke apart, indicating acid attack on the binder.

To select the best acid regenerate which does not harm the binder, we measured the amount of Ca^{+2} in solution after shaking either 500 mg of Ca-titanate or cured cement (without an exchanger) in test solutions for 72 hours. The calcium titanate was made by shaking sodium titanate in a 2 M solution of CaCl_2 for several days. The test solutions were made from different concentrations of acetic acid, nitric acid, nitric acid plus 1 M NaCl, and NaCl. For each type of solution, lower pH's removed more Ca^{+2} from the titanate. Below pH 5.5, nitric acid mixed with 1 M NaCl is the best regenerant, removing the most calcium from calcium titanate. Acidic conditions are required to displace Ca^{+2} with H^{+1} . The presence of NaCl further enhances the amount of Ca^{+2} released by increasing the ionic strength of the solution, thereby increasing the driving force for calcium to leave the exchanger.

The same solutions tested with the Ca-titanate were tested with cured cement containing no exchanger. Regardless of the solution, the cement broke apart when the $\text{pH} \leq 2$. For $\text{pH} \geq 3$, the cement released very little Ca^{+2} for all solutions except acetic acid. Based on these observations, a solution of 0.01 M nitric acid plus 1 M NaCl (initial $\text{pH}=3.1$) is the best regenerant.

Also evaluated were procedures to regenerate bound Na-titanate (assumed to be both the

Ca and Na form) into a form with a larger amount of Na using a two step procedure. For the first step, a solution of 0.01 M nitric acid plus 1 M NaCl was passed through a column packed with sodium titania bound with 50 wt% Cement Fondu-XR (sample 16-1). The acid solution was passed through the column until the effluent pH reached 4 (about 350 column volumes).
5 Next, half of the acid-washed sample was treated with 82 mL 0.1 M NaOH, and the other half with 68 mL of 2 M NaOH. All samples maintained mechanical strength after the treatments.

The untreated sample, the acid washed sample, and the 0.1 M NaOH treated sample all have nearly the same strontium uptake (K_d between 161-264 mL/g based on sodium titanate weight within the pellet). However, the strontium uptake of the sample regenerated with the 2
10 M NaOH was 3.9 times higher than the original sample (623 vs 161 mL/g).

The low K_d of the regenerated bound sample with respect to the virgin sodium titanate powder (623 vs. 10,000 mL/g) probably indicates that mass transfer within the pellet must be improved by increasing the porosity.

EXAMPLE 18

Partially crystalline layered sodium titanate unbound and bound with 50 wt% Cement Fondu was tested for radiation stability. The samples were irradiated for 250, 500, 750 and 1000 Mrad of exposure. All of the sodium titanate powders exhibited a K_d of approximately 40,000 ml/g. The Sr- K_d values of the irradiated bound samples are all equivalent with a value of 150 ml/g, which is consistent with the values seen in Table 9. The unirradiated sample had a slightly higher K_d and may be within experimental error of the analytic technique. All of the bound samples qualitatively exhibited excellent mechanical strength after irradiation and treatment with caustic.

10

EXAMPLE 19

In this Example, sodium titanate gel was tested as a binder for partially crystalline sodium titanate and found to have good mechanical strength, is resistant to caustic, and enhances the strontium uptake of sodium titanate. Since the sodium titanate gel is inorganic, this binder
5 will have a high resistance to damage by radiation.

Sodium titanate as prepared in Example 5 was bound with sodium titanate gel by two different methods. In the first method according to Example 12, the binder was formed by making a sodium titanate sol-gel (methanol, NaOH, and titanium isopropoxide) and adding the sodium titanate exchanger before curing. In the second and preferred method according to
10 Example 13, titanium isopropoxide (TiP) was mixed with the sodium titanate ion exchanger and allowed to solidify in moist air before curing.

Table 14 summarizes the effectiveness of titanate as a binder for sodium titanate with respect to ion exchange capacity and mechanical strength. Bound samples passed the mechanical test if they withstood being shaken for 24 hours in solutions containing 64 ppm Sr, 5 M NaNO₃,
15 and 0.1 M NaOH (marked as "P" in Table 14). Those that failed are designated by "F".

The presence of the titanate binder enhances strontium uptake by sodium titanate. Compared to the unbound sodium titanate (19-1), samples 19-2 and 19-3, bound with the gel method, took up 1.76 times more strontium; and sample 19-6, bound with the TiP method, took up 2.9 times more strontium. Amorphous sodium titanate (gel) by itself gives a high K_d for Sr
20 (17,000 mL/g). The high strontium K_ds may be the result of a combination of the binder enhancing mass transfer and the powder having a high capacity for strontium.

TABLE 14
Strontium Uptake by Sodium Titania bound with Amorphous Sodium Titanate.
Bound samples 20-40 mesh -- Feed 64 ppm Sr/5.1 M NaNO₃/0.1 M NaOH

Sample	Binder	Form	Curing Method	Mechanical Strength*	K _d mL/g
19-1 (batch 2)	none	powder	----	---	10,930
19-2	gel	plaque	6 days in air at room temperature	P	19,220
19-3	gel	extrudate	6 days in air at room temperature	P	19,220
19-4	gel	extrudate	4 days in water at room temperature; 85°C in air overnight	F	—
19-5	TiP	plaque	2 days in air at room temperature	F	---
19-6	TiP	plaque	85°C in air overnight	P	31,800

EXAMPLE 20

This example details the measurement of strontium equilibrium batch capacities for titania bound Na-titanate prepared according to Example 13, as well as each of the unbound pilot plant batches prepared in Example 5. As shown in Table 15, the 24-hour K_d of titania bound sodium titanate is 3.5 times higher than powder (37,000 vs. 10,800 mL/g for 64 ppm Sr, 5.1 M NaNO_3 , and 0.1 M NaOH). However, the capacity of the TiP-bound sodium titanate is nearly the same as for the unbound material (batch 2). Because the presence of the titania binder does not affect capacity, the binder itself may take up strontium. K_d measurements of the titania binder indicates that this is the case, with a K_d of 17,000 mL/g (64 ppm Sr, 5.1 M NaNO_3 , 0.1 M NaOH). The powder combined with the binder has a higher strontium uptake than the powder of the binder by itself. The titania binding process produces a composite material which has enhanced mass transfer.

TABLE 15

Capacities of Strontium Exchangers. Feed: 55.4 ppm Sr, 5.1 M Na, 0.1 M OH.

Exchanger	Capacity (meq/g)	K_d (mL/g)
Na-Titanate pilot plant batch 1	0.897	12,100
Na-Titanate pilot plant batch 2	1.06	10,800
Na-Titanate pilot plant batch 3	1.112	14,800
Na-Titanate pilot plant batch 4	1.19	21,000
Na-Titania bound with amorphous Na-titanate	0.991	37,000

EXAMPLE 21

This Example details a method for manufacturing sodium titanate ion exchange pellets using an organic binder with introduced porosity to improve mass transfer inside the pellet. Partially crystalline sodium titanate powder produced in Example 5 had a Sr^{2+} distribution coefficient (K_d) of 16900 mL/g. The sodium titanate powder was subsequently bound with 20 wt % cellulose acetate. While K_d testing on the preliminary pellets were positive (K_d Ca 2500), later pellets consistently tested low with K_d values less than 300. The extreme decrease in K_d was due to decreased mass transfer through the cellulose acetate. Incorporating porosity in the pellet using a binder with pore former, consistently recovered the K_d to values greater than 1600 mL/g.

The process to produce pellets with pore former consisted of dissolving cellulose acetate (22.5 wt %) in an acetone (47.5 wt %)/formamide (30.0 wt %) mixture. Pores are formed by a phase inversion of the acetone/formamide/water system when the pellet is later extruded into water. The solution was blended with sodium titanate at a weight ratio of 1:4 cellulose acetate to ion exchanger. Once blended, the mixture was stirred to volatilize enough acetone to leave a thick paste. The paste was extruded into a water wash bath containing 0.1% Triton XL-80N, 50% glycol and 25% glycerol at 10°C. The purpose of the water bath is to leach the formamide/acetone solvent and to minimize the pore collapse due to drying of the membrane. The low temperature facilitates the precipitation of the polymer and freezing of the pore structure. The surfactant reduces pore collapse upon drying by reducing capillary pressures.

The reason for the loss of mass transfer upon binding is apparent from Table 16. The

surface area of virgin sodium titanate is greater than 139 m²/g, but the extruded powder blended with cellulose acetate and acetone showed very little surface area (< 1 m²/g). The cellulose acetate had blinded the surface of the sodium titanate powder. By using the pore former solution and a cooled surfactant water bath, the surface area increased to greater than 91 m²/g.

- 5 Additionally, the wettability of the pellets using the new binder process also increased. The pellets with pore former wetted more easily due to intact pores and presence of residual surfactant in the pores.

TABLE 16

Sodium Titania bound With -	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Average Pore Radius (Å)	Langmuir Surface Area (m ² /g)	Wetability Testing (5 min)
Ca-Montmorillonite Powder	82.2	0.163	39.6	139.6	
Cellulose Acetate	<1	-	-	<1	-
20 wt % Cellulose Acetate/Acetone Air Dry - 23°C	<1	-	-	<1	Very Little Penetration
20 wt % Cellulose Acetate/Acetone 10°C Quench - Air Dry	57.6	0.116	40.2	100.1	1/4 Dia. Wetted
20 wt % Cellulose Acetate/Acetone/ Formamide 10°C Quench - Air Dry	52.8	0.108	40.8	91.9	Complete
20 wt % Ethyl Cellulose/Propanol 10°C Quench - Air Dry	48.8	0.102	41.8	86.9	1/8 Dia. Wetted

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EXAMPLE 22

This example demonstrates that heat treatment increases the mechanical strength of titania bound sodium titanate. When partially crystalline sodium titanate is mixed with a hydrolyzable titanium compound in air and stirred for about one hour, a paste like material is obtained due to the hydrolysis of TiP to form titania/titanium hydroxide. This material was then cured at room temperature in air and then dried at 90°C overnight. After drying the material was ground to below 40 mesh. The titania bound sodium titanate powder was compressed in a pelletizer to a piece density of 1.8 - 2.2 g/ml. The pellets were then calcined at 200°C, 300°C and 400°C, respectively. After 4 hours of thermal treatment, the pellets were crush tested using the ASTM method D4179. The physical properties of the crushed product were combined with product AW-300 zeolite, manufactured by Des Plaines, Illinois, UOP. The instrument used was an Instron model 4502 with a 100 Newton load cell. The results are found in the following Table 17.

TABLE 17

	Tip-bound Sodium Titanate Pellets	AW-300 Pellets
Radial stress at maximum	519 PSI	343 PSI
Axial stress at maximum	2354 PSI	-----

All the calcined titania bound sodium titanate pellets have very good mechanical strength with strong resistance against degradation in alkali solution. The strontium distribution constants

(Kds) for these pellets were measured both as intact pellets and after crushing to 40-100 mesh.

These results are found in Table 18.

TABLE 18

Tip Bound Material	Strontium Kd
Calcined at 200°C, 40-100 mesh	21531 mL/g
Calcined at 200°C, intact pellets	24063 mL/g
Calcined at 300°C, 40-100 mesh	19079 mL/g
Calcined at 300°C, intact pellets	3661 mL/g
Calcined at 400°C, 40-100 mesh	17114 mL/g
Calcined at 500°C, intact pellets	20000 mL/g
Uncalcined, 40-100 mesh	51181 mL/g
Uncalcined, intact pellets	59014 mL/g

EXAMPLE 23

Partially crystalline sodium titanate made according to the method of Example 5 was added to a slurry of hydrous titania. Methyl cellulose was added as organic binder to form the material before calcination. The mixture was extruded and calcined at 560°C for 4 hours. The
5 calcined extrudates exhibited good mechanical strength, but powdered in alkali solution.

EXAMPLE 24

Partially crystalline sodium titanate made using the method described in Example 5 was mixed with titania hydrate powder. The mixture was pelleted to a piece density of 1.8 - 2.2 g/ml. The pellets were then calcined at 400°C and 560°C, respectively. After 4 hours of thermal treatment, calcined extrudates have reasonably good mechanical strength, but powdered in alkali solution.

EXAMPLE 25

The titania bound sodium titanate powder made using method describing in Example 13 was mixed with titania hydrate powder. The mixture was pelleted to a piece density of 1.8 - 2.2 g/ml. the pellets were then calcined at 400°C and 560°C, respectively. After 4 hours of thermal treatment, all the pellets have very good mechanical strength with strong resistance
5 against degradation in alkali solution.

EXAMPLE 26

This example demonstrates a process of making titania bound crystalline sodium titanate pellets using a motorized pellet former, which is facilitated by the presence of a solid lubricant, namely stearic acid. The titania bound crystalline sodium titanate powder was mixed with 0.5%
5 - 4% of stearic acid and pelletized with tablet press, Coulton 215, to a piece density of 1.8 - 2.2 g/ml. The pellets were then calcined at 400°C either in the air or in air saturated with moisture at room temperature. After 4 hours of thermal treatment, all the pellets have very good mechanical strength with strong resistance against degradation in alkali solution.

The strontium Kd was measured for three samples: intact pellets; pellets ground to 16-45
10 mesh; and to below 45 mesh. The intact pellets had a K_d of 11,860 mL/g. The 16-45 mesh material has a K_d of 11,531, and the 45+ mesh material had a K_d of 12,813.

EXAMPLE 27

In this example, titania bound crystalline sodium titanate prepared by the method of Example 13 is used to remove uranium from an aqueous solution.

200 mg of 20-40 mesh titania bound sodium titanate pellets were placed in a beaker. A
5 25ml solution comprising 50ppm uranium was contacted with the solid sodium titanate for 24
hours. The solution concentration of uranium after 24 hours was 3ppm. This translates to a
uranium Kd of over 1600 mL/g.

EXAMPLE 28

This example describes a method for converting partially crystalline sodium titanate into crystalline hydrogen titanate followed by testing the hydrogen titanate as an ion-exchanger.

10 grams of partially crystalline sodium titanate prepared as in Example 5 was added to
5 a liter solution of 0.1 N HNO_3 . The mixture was shaken for 18 hours during which time the solution pH increased from about 1.38 to about 1.46. The solids were filtered from the solution, recovered, and dried. The resulting crystalline hydrogen titanate was tested for its ability to exchange various metal ions and the ion-exchange test results are reported in Table 19.

TABLE 19
Hydrogen Titanate Ion Exchange Capacities

Target Metal	Initial Concentration (ppm)	K _a (mL/g)
Yb	78	38900
Zr	51	12650
Mo	11	10900
Ag	19	9400
Ti	17	5566.667
Pb	5.6	5500
Cr	4.3	5280
V	20	4900
Fe	15	4900
Cs	19.7	4280
Sn	26	2790
Sb	20	2500
As	19	1800
Y	18	1190
Cd	20	614.2857
K	29	400
Hg	18	386.4865
Cu	24	352.8302
Ba	3.6	350

TABLE 19 Cont.
Hydrogen Titanate Ion Exchange Capacities

5	Rb	19	273
	Sr	20	156.4103
	Zn	18	80
	Pd	18	64
	Co	25	17.05882
10	Ni	23	43.75
	Al	26	30
	Pt	18	29
	Mg	19	26.3337

15

Solution pH = 2-3

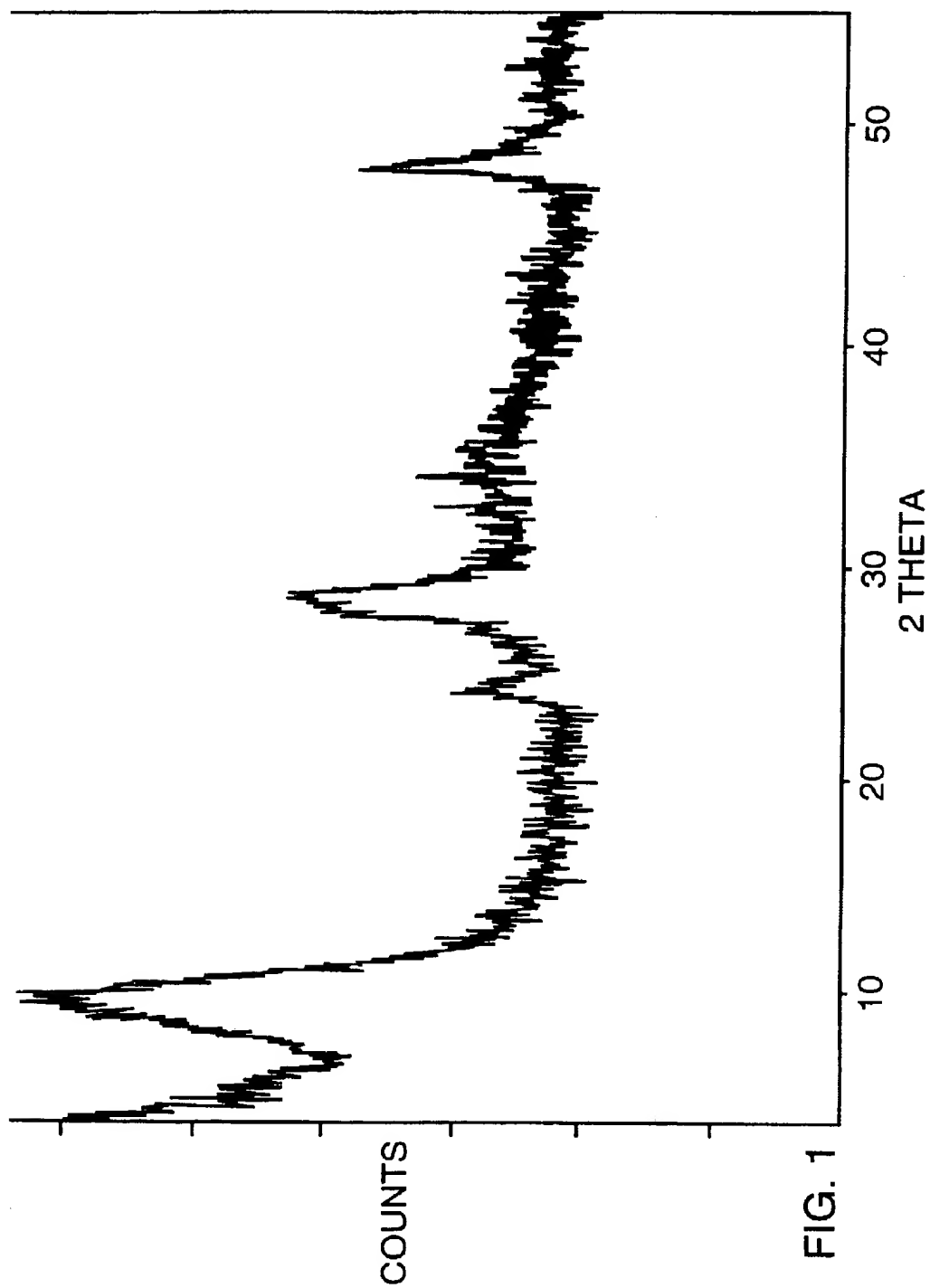
What We Claim Is:

1. A layered partially crystalline sodium titanate having a d-spacing of from 8 to 9.9 angstroms.
2. The layered partially crystalline sodium titanate of claim 1 having a surface area
5 of from about 25-200 m²/g.
3. The layered partially crystalline sodium titanate of claim 1 having the X-ray diffraction pattern of Figure 1.
4. The layered partially crystalline sodium titanate of claim 1 having a d-spacing of from 9.0 to 9.9 angstroms.
- 10 5. The layered partially crystalline sodium titanate of claim 1 having a (001) reflection peak half width greater than 2° and less than about 4.5°.
6. The layered partially crystalline sodium titanate of claim 1 having a 24 hour K_d for strontium of at least 20,000 mL/g based on a solution consisting of 55ppm Sr/5 M NaNO₃/0.1 M NaOH.
- 15 7. The layered partially crystalline sodium titanate of claim 1 having the formula $\text{Na}_{3.4-4.4}\text{Ti}_{8.4-9.2}\text{O}_{18.5-20.6}$.
8. An ion exchange material comprising from about 40 to about 95 wt % of the layered partially crystalline sodium titanate of claim 1 and from about 5 to about 60 wt % of a binder.
- 20 9. The ion exchange material of claim 8 wherein the binder is an organic binder selected from the group consisting of polymers, starches, cellulose, and cellulose acetate.

10. The ion exchange material of claim 8 wherein the binder is an inorganic binder selected from the group consisting of: silica, clays, silicates, ceramics, alumina, titanium dioxide, zirconium dioxide, chromium oxide, beryllium oxide, vanadium oxide, cerium oxide, hafnium oxide, zinc oxide, magnesia, boria, thoria, silica-alumina, silica-magnesia, chromia-
5 alumina, alumina-boria, silica-zirconia, and crystalline zeolitic aluminosilicates.
11. The ion exchange material of claim 8 wherein the binder is cellulose acetate.
12. A layered partially crystalline sodium titanate having a d-spacing of from 8.5 to 9.9 angstroms, a surface area of from 25 to 200 m²/g, and (001) reflection peak half width greater than 1° and less than about 4.5°.
- 10 13. A layered partially crystalline sodium titanate having the x-ray diffraction pattern of Figure 1 prepared by hydrothermally treating a sodium titanate gel at a temperature of from about 120°C to about 200°C in the presence of NaOH.
14. The layered partially crystalline sodium titanate of claim 13 wherein the hydrothermal treatment occurs for a period of time ranging from about 1 to about 20 hours.
- 15 15. The layered partially crystalline sodium titanate of claim 13 wherein the sodium titanate gel is prepared by a method selected from the group consisting of the sol-gel method and the reflux method.
16. A layered partially crystalline sodium having a d-spacing of from 9.0 to 9.9 angstroms, a surface area of from 60 to 110 M²/g, and (001) reflection peak half width greater
20 than 2° and less than about 4.5° prepared by the method comprising hydrothermally treating a sodium titanate gel prepared by the reflux method at a temperature of from about 150°C to about

170°C in the presence of NaOH for a period of time ranging from about 1 hour to about 5 hours.

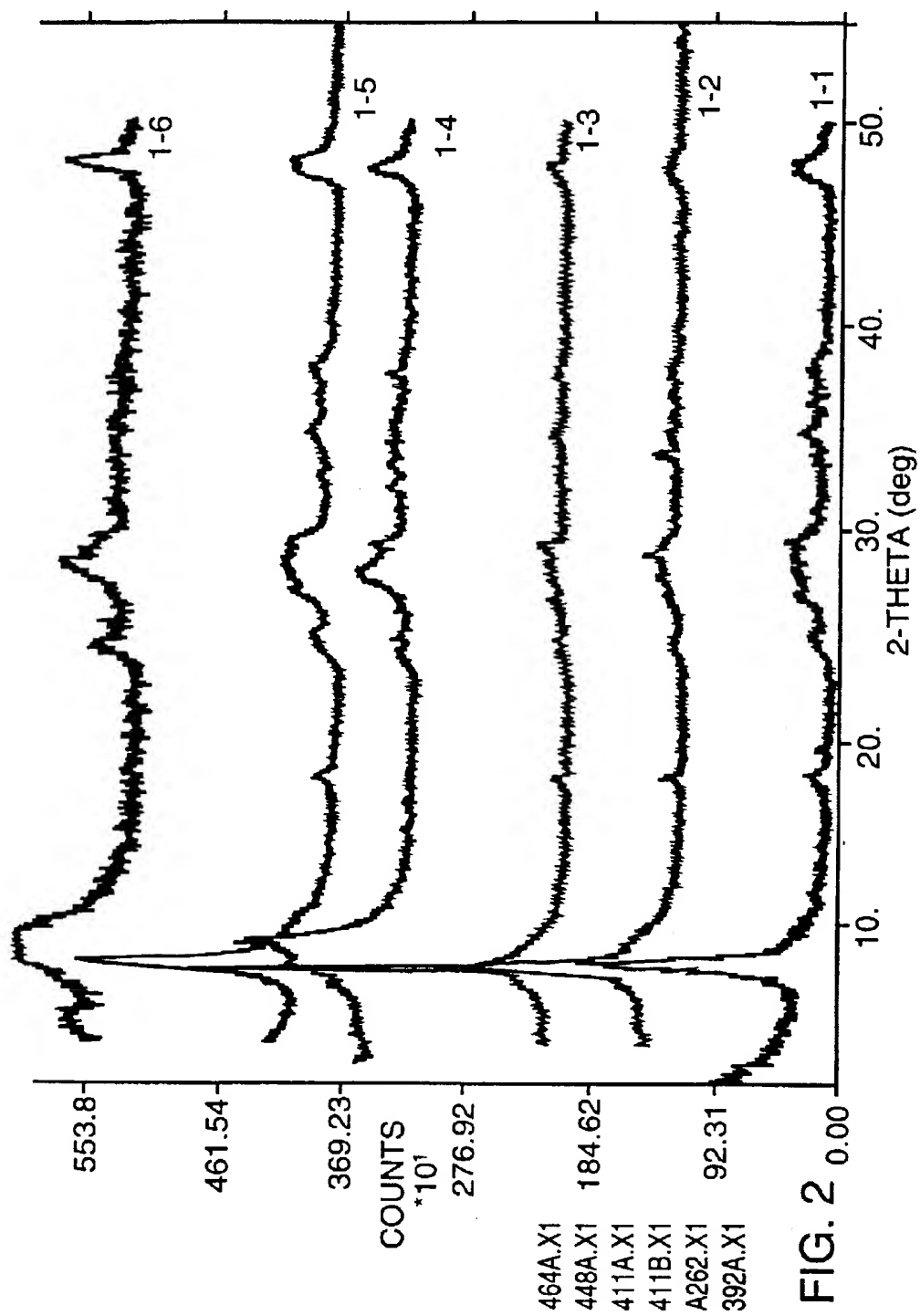
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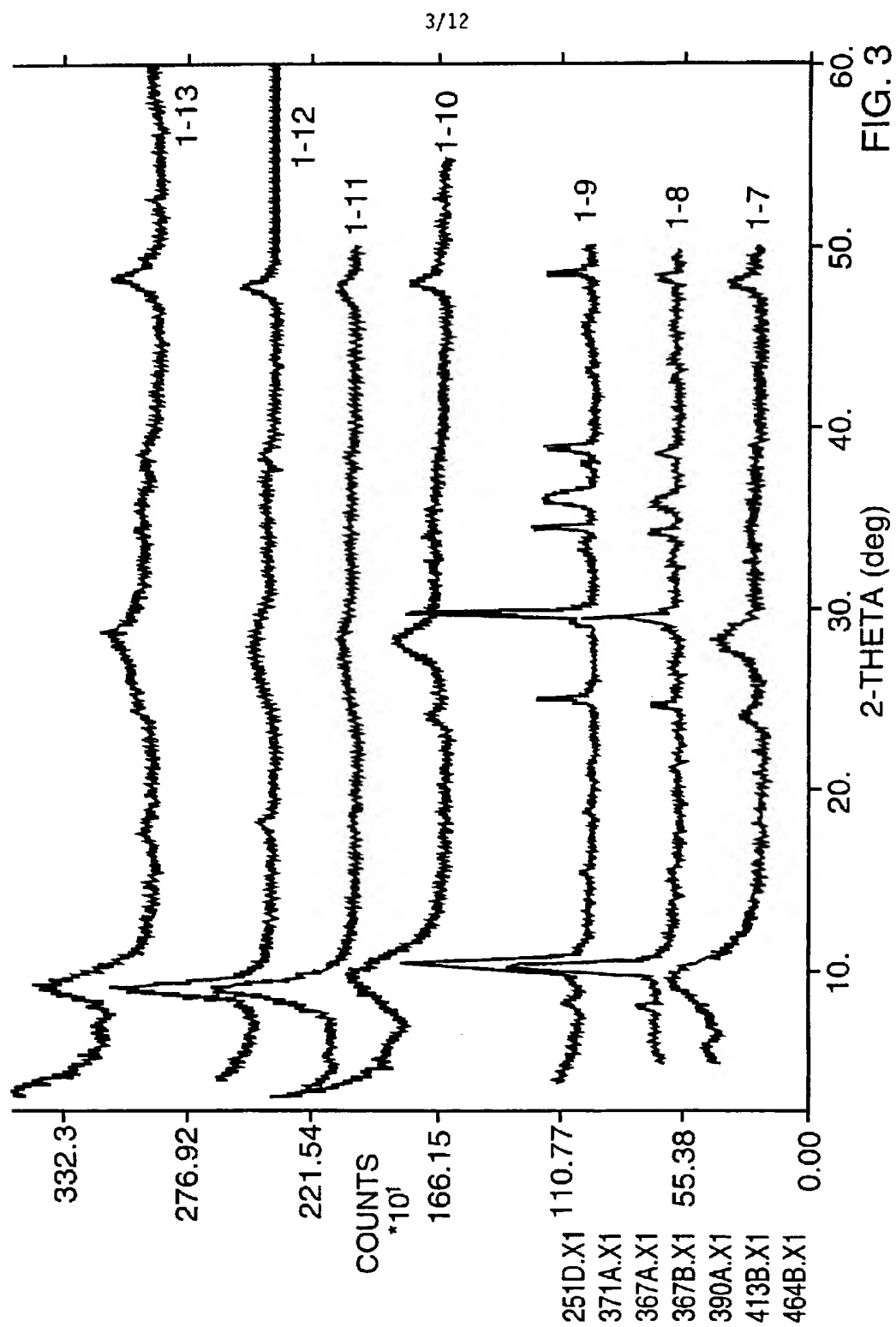
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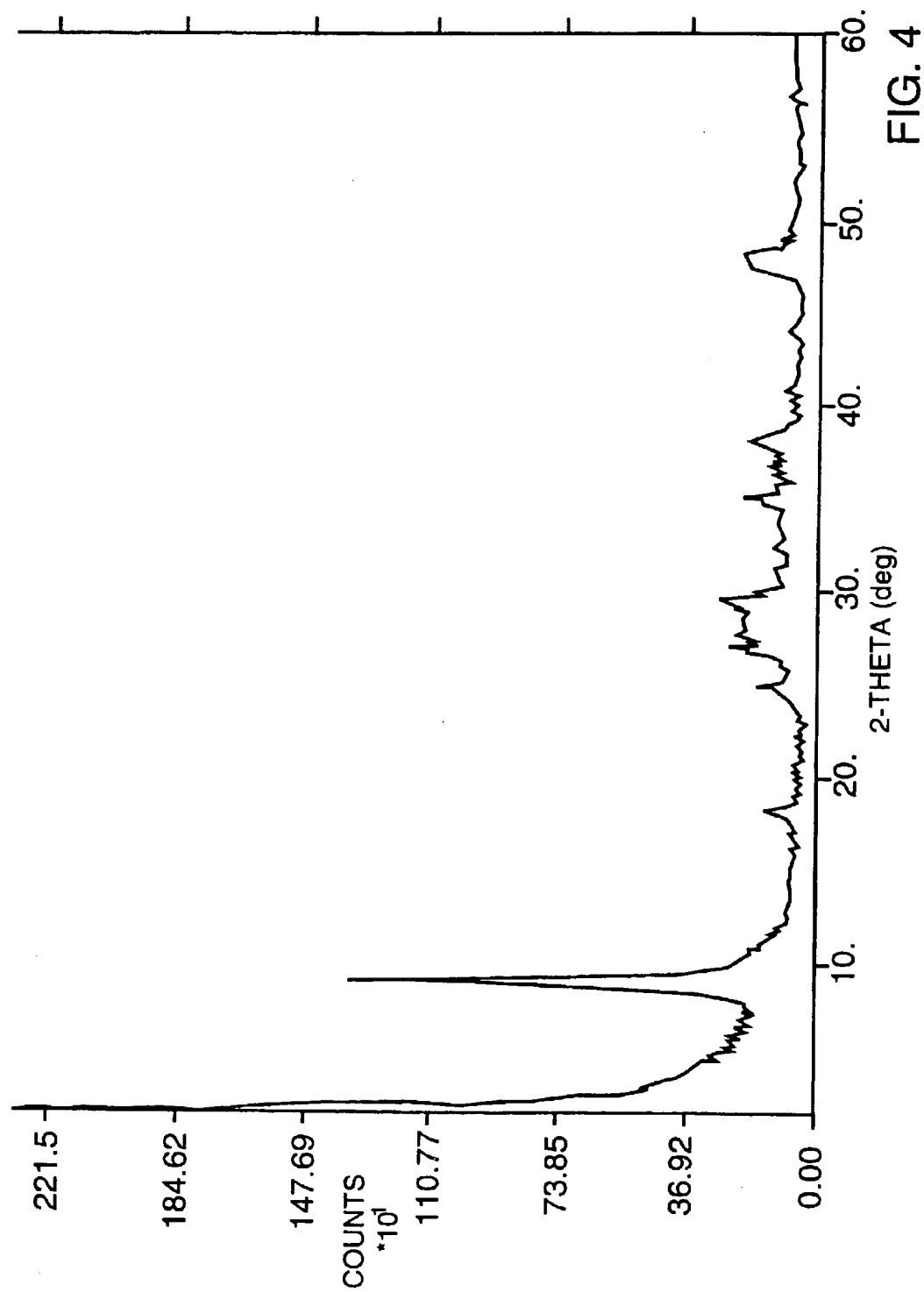
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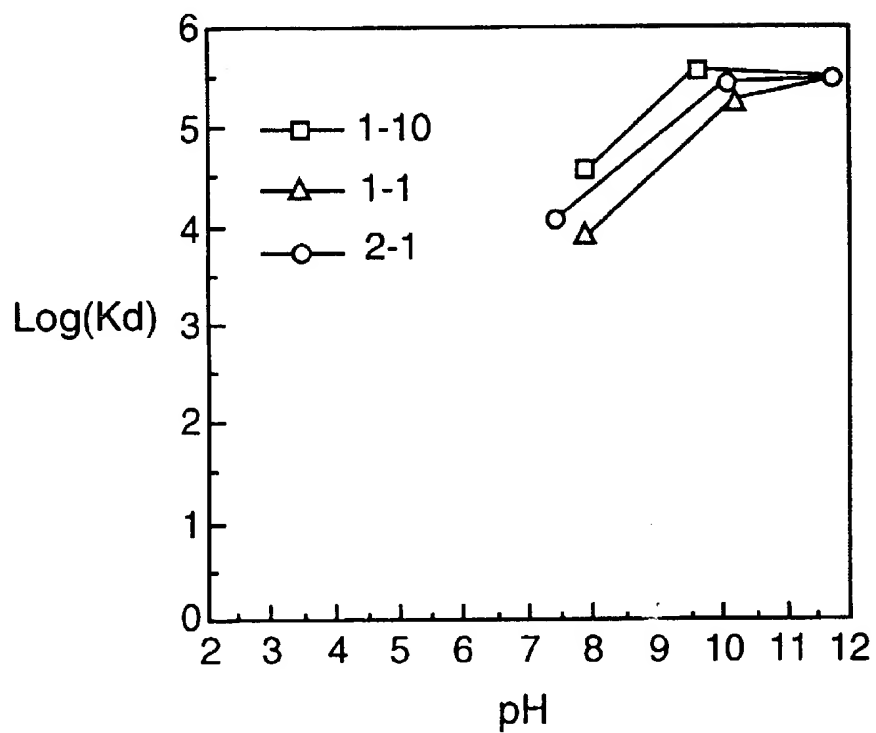
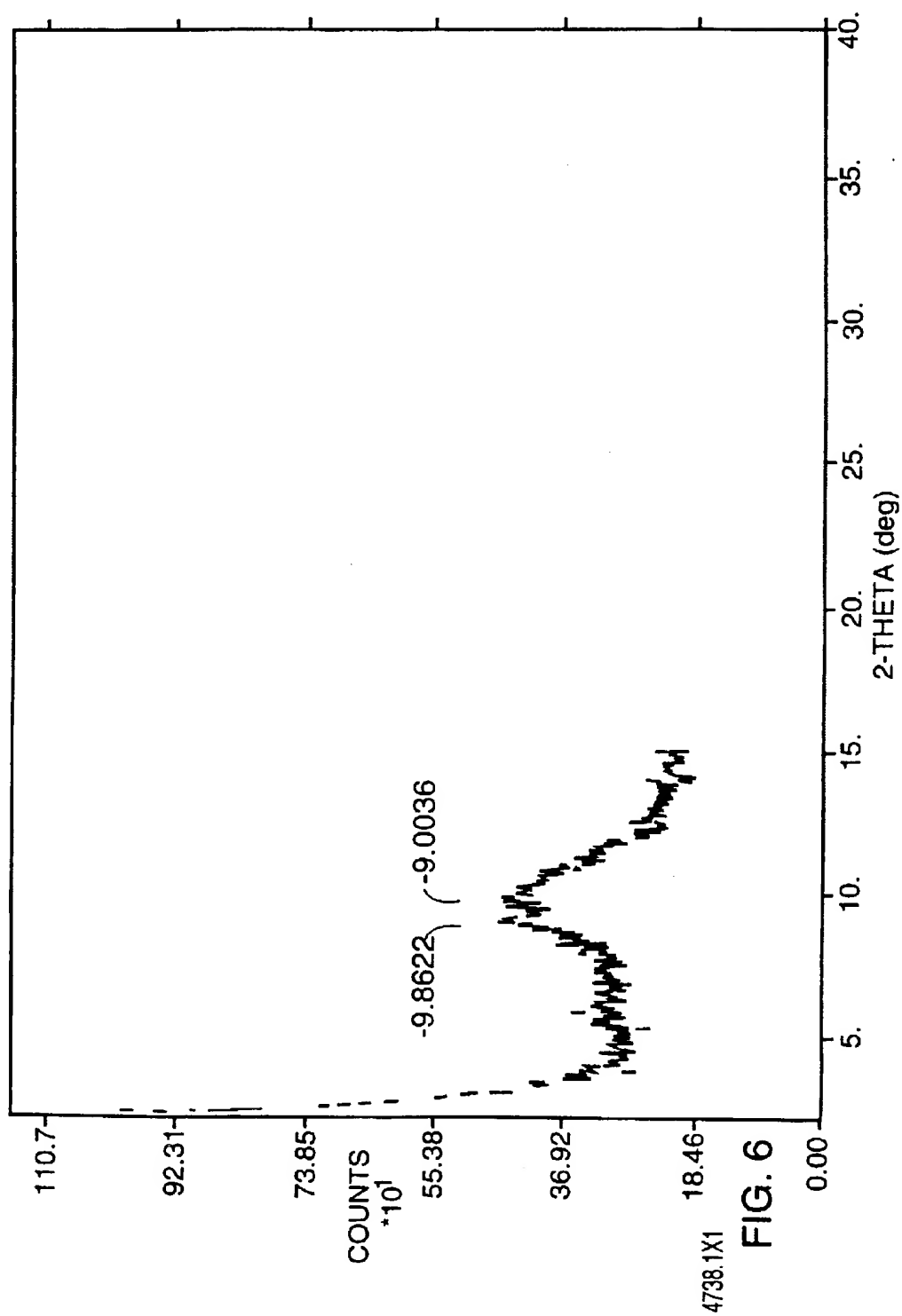


FIG. 5

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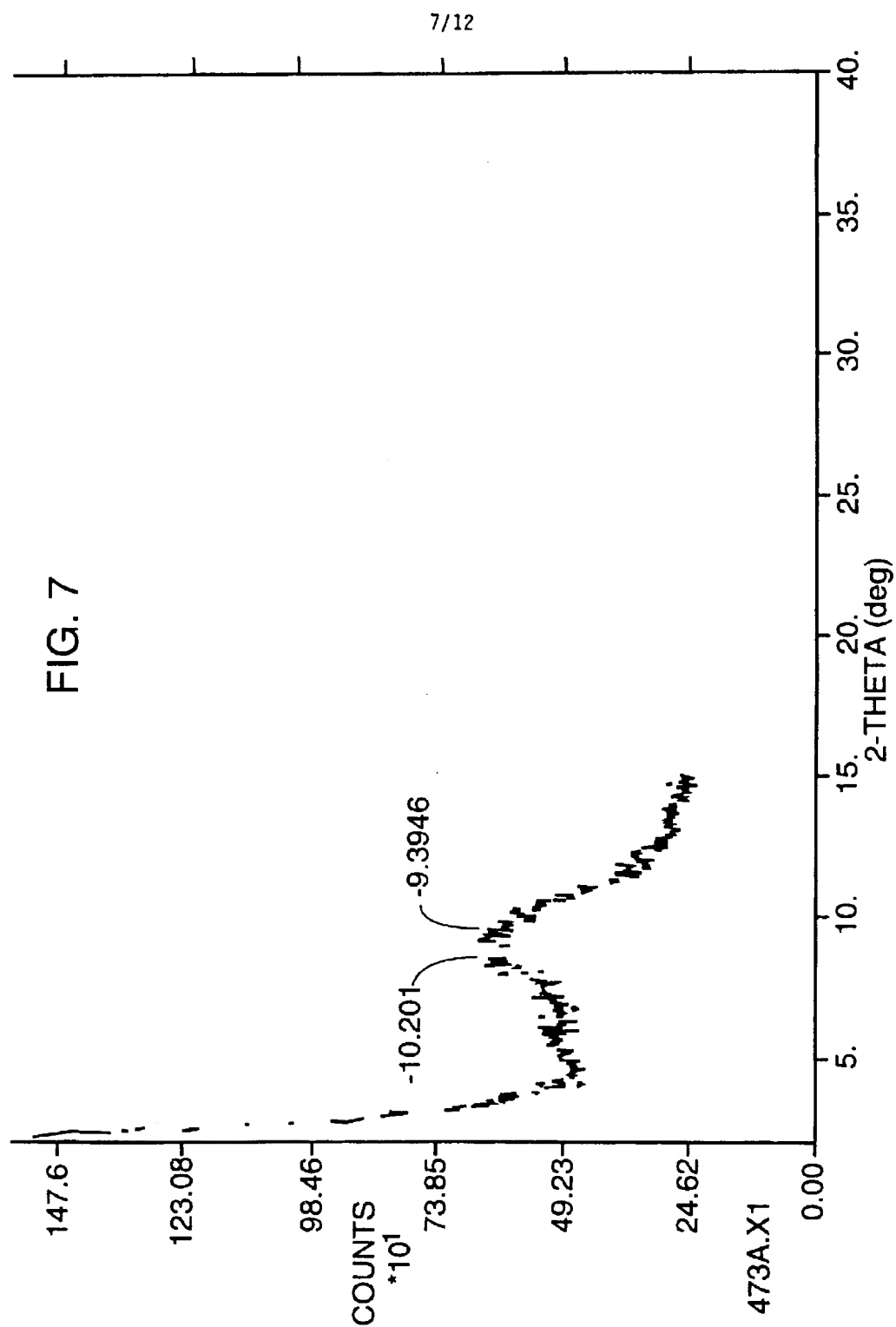
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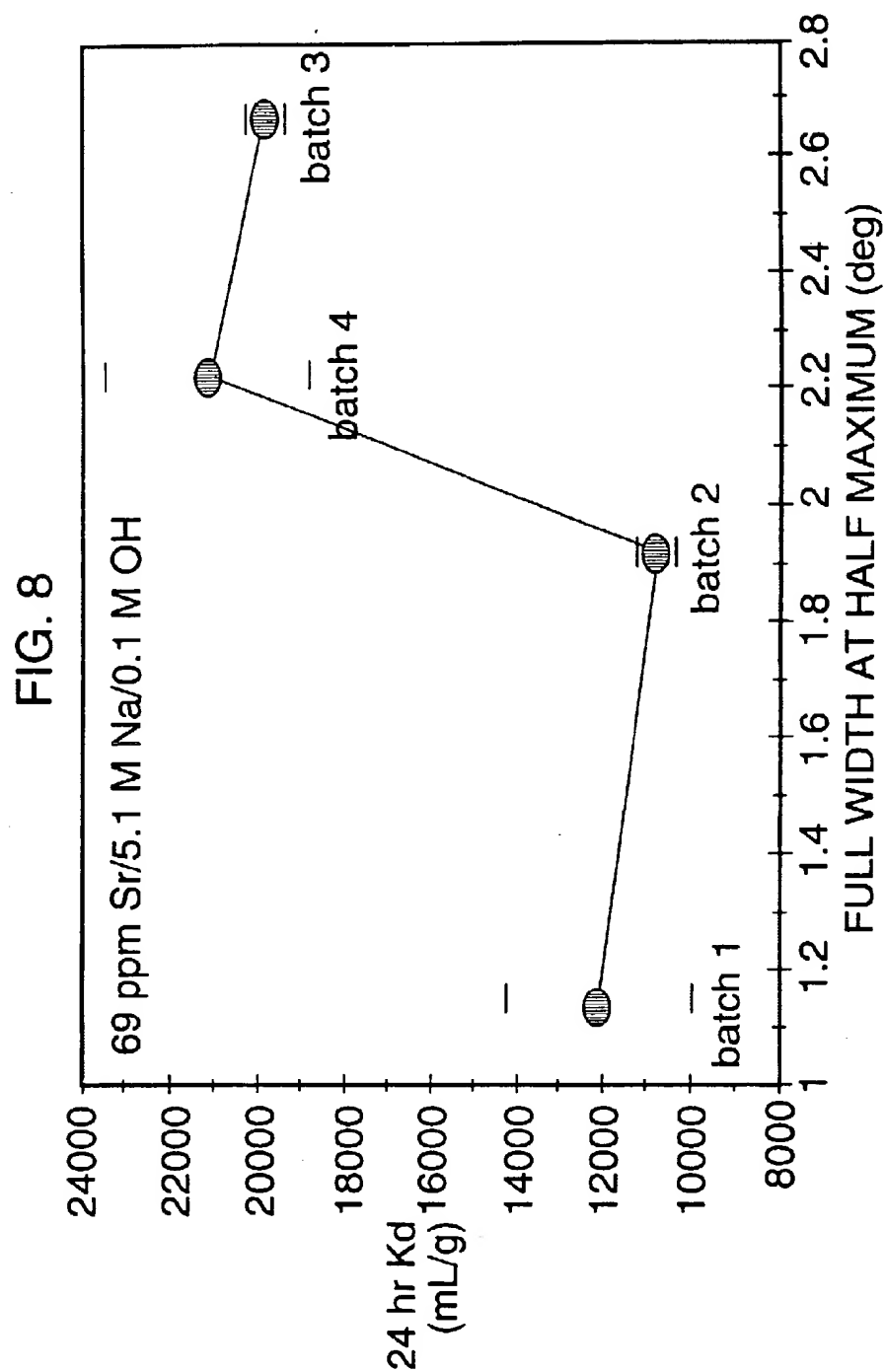
WEST



SUBSTITUTE SHEET (RULE 26)

WEST

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SUBSTITUTE SHEET (RULE 26)

WEST

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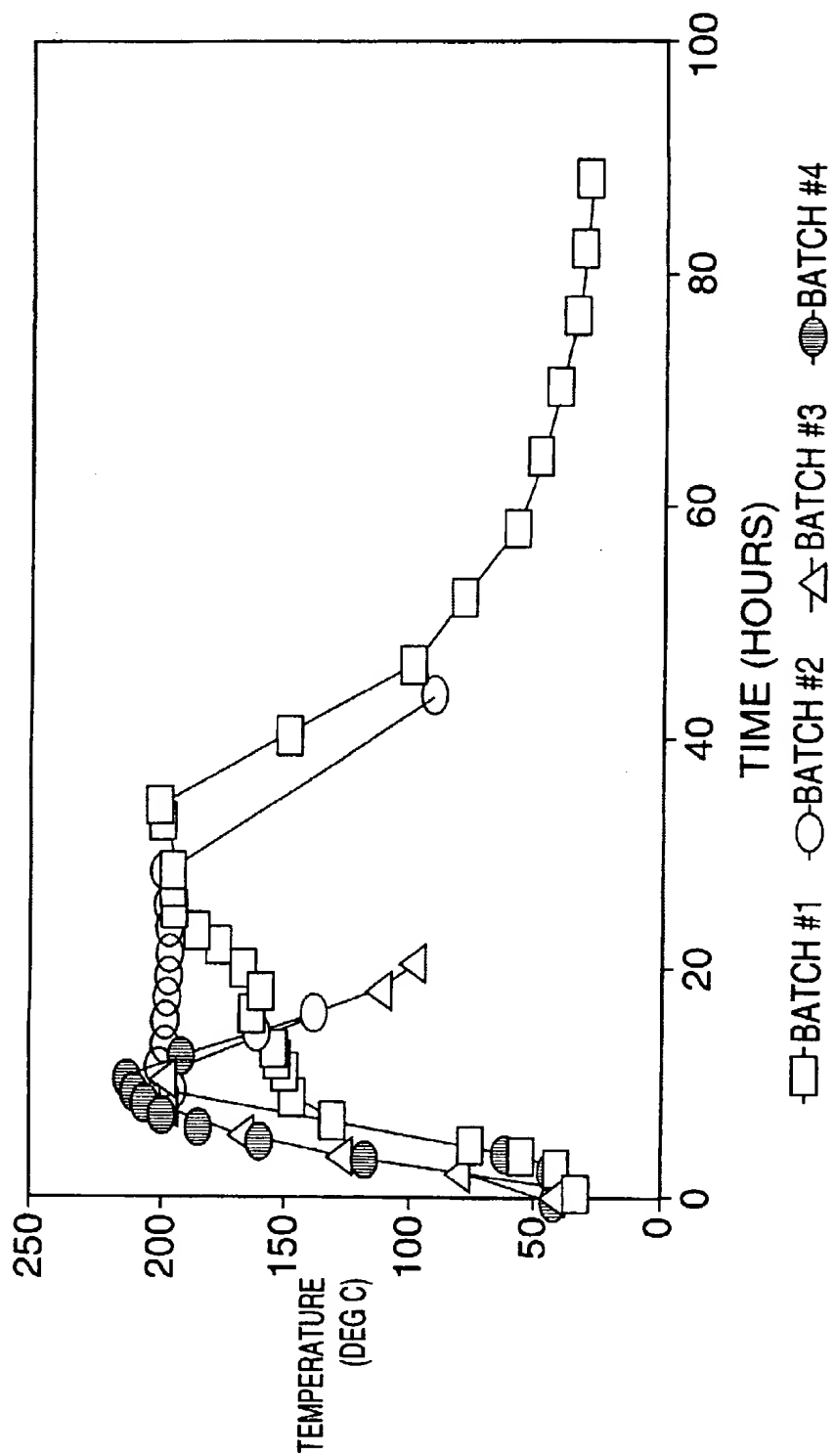


FIG. 9

SUBSTITUTE SHEET (RULE 26)

WEST

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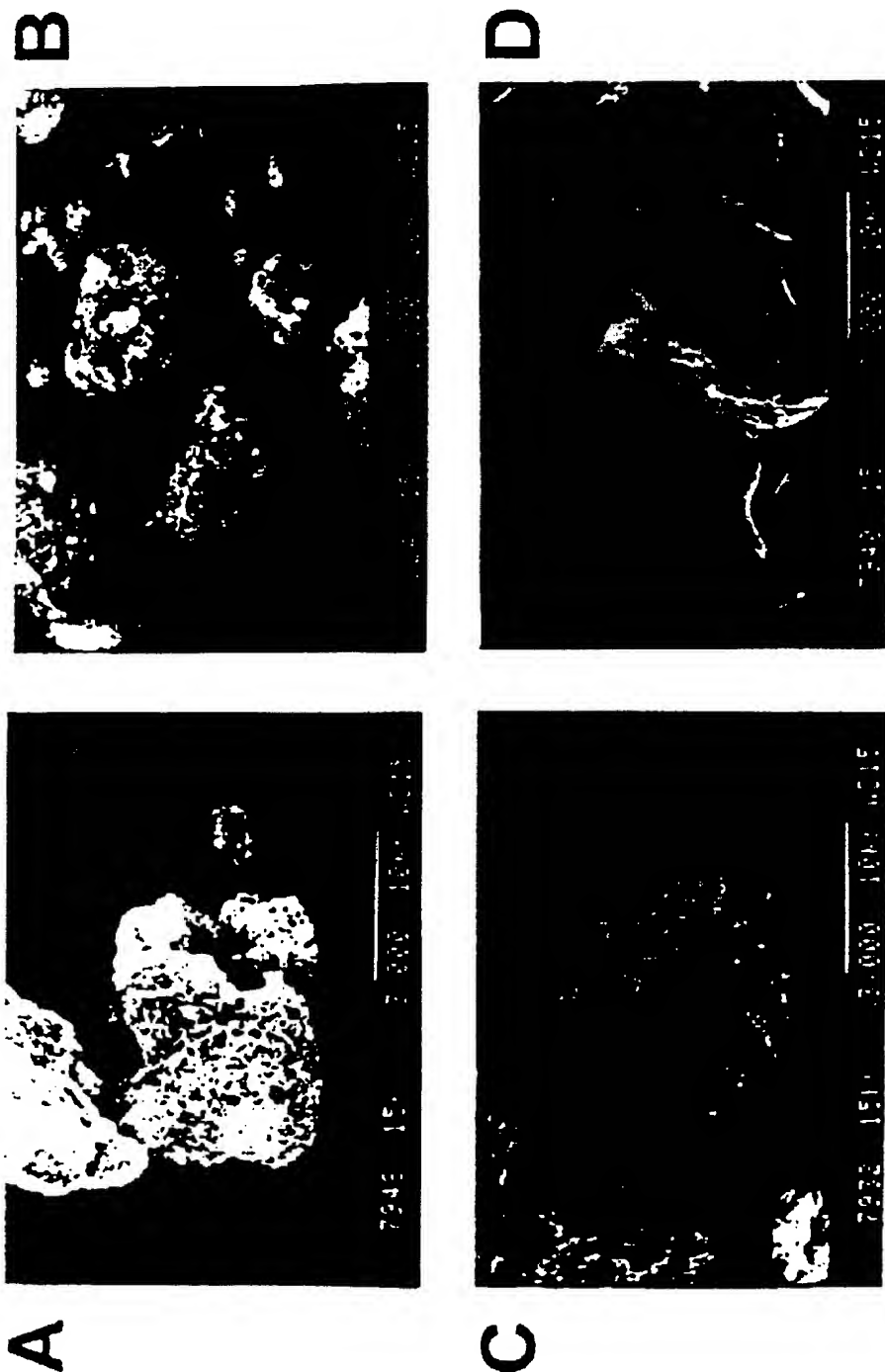


FIGURE 10

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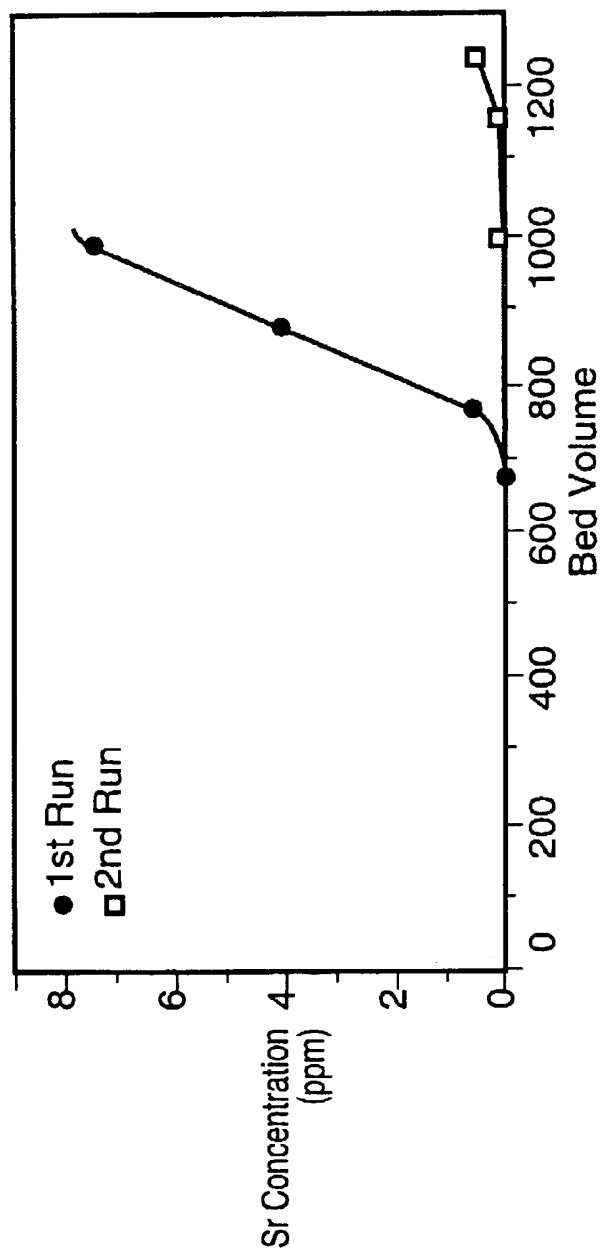


FIG. 11

SUBSTITUTE SHEET (RULE 26)

WEST

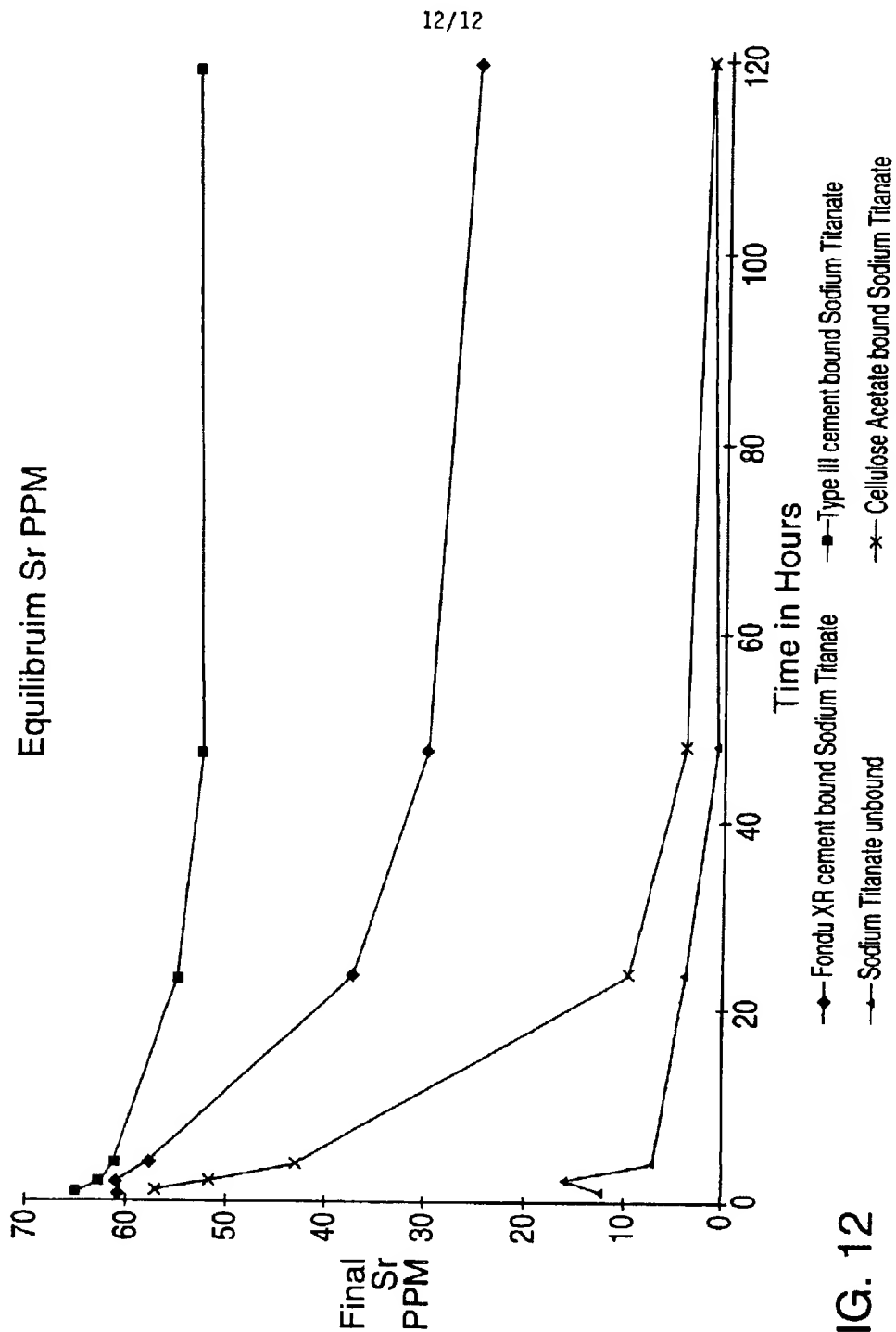


FIG. 12